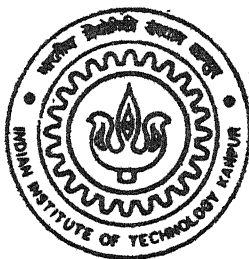# PROCESSING OF SiC AND CELSIAN USING ORGANIC PRECURSORS

by

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January, 2000

PROCESSING OF SiC AND CELSIAN USING ORGANIC PRECURSORS

A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF TECHNOLOGY

by

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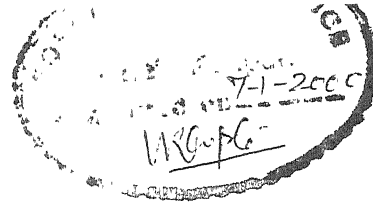**JAN 2000**

Certificate

This is to certify that the present work, entitled "**Processing of SiC and Celsian using Organic Precursors**" by **Miss. R. Bindu (Roll No: 9810615)** has been carried out under our supervision and to the best of our knowledge it has not been submitted elsewhere for a degree.

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Acknowledgement

I place on record my deep sense of gratitude to Dr. V. S. R. Murthy and Dr. V. Chandrasekhar for their timely advice, constant encouragement and kind cooperation throughout the course of this investigation.

I am thankful to all the members of the Department of Materials and Metallurgical Engineering, Department of Chemistry, Advanced Centre for Materials Science and Laser Raman Lab.

I am very thankful to Mr. V. Krishnan for helping me whenever I needed help. I also thank my other labmates Mr. G. T. S. Andavan, Mr. A. Athimoolam, Mr. S. Nagendran, Mr. R. Boomishankar, Mr. S. Kingsley and Mr. V. Bhaskar for being cooperative and helpful.

I take this oppurtunity to thank my Father, Mother and my Brother. Life wouldn't have been comfortable without their blessings and meticulous care. I dedicate my thesis to them.

Then remains the pleasant task of acknowledging a number of friends from the Department of Materials and Metallurgical Engineering, Department of Chemistry and Girls Hostel, to be candid, itemizing their names would be nothing compared to what I got from them.

Synopsis

Small diameter SiC fibers produced by polymer precursor route are widely used for reinforcement of metallic, intermetallic and ceramic matrix composites. Until now, SiC has been produced from a large number of precursors like polysilanes and polycarbosilanes. The synthesis of these precursors involve a minimum of two steps. In this study a new method involving the use of divinylbenzene as the crosslinking agent has been explored by which the ceramic precursors viz., polysilanes were produced in a single step. Pyrolysis of these polymers at 1500°C for 8 hour resulted in the formation of β-SiC, which was characterized using a number of techniques.

In the second part of this work, a refractory phase based on barium aluminosilicate(e.g. celsian) composites has been produced. Celsian is considered as a potential precursor matrix material for high temperature composites due to its high melting temperature and good oxidation resistance. Additionaly, the monoclinic form of celsian has low thermal expansion and excellent phase stability upto 1590 °C. Although monoclinic celsian is a thermodynamically stable phase up to 1590 °C, metastable hexacelsian readily crystallizes from stoichiometric glass-ceramic upon solidification of conventional melts. In this investigation, the formation of hexacelsian has been suppressed by using sol-gel method where a number of seeding techniques were tried. The desired monoclinic phase could be stabilized by addition of TiO_2, Li_2O or SrO_2. To increase the toughness of celsian based materials, ZrO_2 was added as a reinforcement phase. The added zirconia particles were stable in a tetragonal form. This gives the opportuniy to study the tetragonal to monoclinic martensitic transformation which can be useful for toughening the glass-ceramic matrix.

Contents

List of Tables

List Of Figures

Chapter 1
Introduction

Last decade has seen the development and application of many new structural, electronic, magnetic and optical ceramics. Advanced structural ceramics are associated with engineering applications starting from cutting tools to heat engine components[1*]. For many years, researchers have sought to develop tough ceramics whose performance characteristics retain the best properties of their parent ceramics and have additional quality of not being susceptible to fracture during impact or stress in the presence of a notch. The addition of fibers to the ceramics is known to be an effective approach for achieving this goal. The development of fiber reinforced cement is the best known example of this technology[2]. Early experiments performed in the Europe and United States demonstrated that high performance fibers could be successfully incorporated into glasses to achieve high strength and tough composite materials. Through the use of carbon fiber to reinforce glasses and glass-ceramics, composites with strength above 700 MPa were demonstrated by 1973 but it was not acceptable at that time due to oxidative instability of the carbon fibers[2-6].

More recently it was possible to extend this work because of the availability of new fibers, which permit the creation of composites with superior oxidation resistance. In this context, SiC fibers developed by Yajima and coworkers[7,8] revolutionized the area of structural ceramic composite materials. Originally, SiC fibers (Commercial name-Nicalon; produced by Nippon Carbon Company Limited, Japan) were produced from polycarbosilane (PCS) precursors[9-14]. SiC fibers produced by polymer precursor method are light in weight and exhibit high strength, elastic modulus and smooth fiber surface. It is resistant to heat and oxidation. It has a small thermal expansion coefficient and the specific resistivity of a semiconductor. It can be woven into various complex shapes. Because of these superior qualities, such ceramic fiber ceramic-matrix composites[15] have high strength and high fracture toughness even at elevated temperatures (up to 1000°C) and are a promising class of structural materials for application where high strength, high stiffness, low thermal expansion, low density, low temperature stability and low radioactivation are desirable

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* - References are given at the end of each Chapter

attributes[5]. The main shortcoming of PCS is that it is unstable at room temperature. Hence there have been efforts to develop several alternative precursors. In this study, alternative stable precursors viz., crosslinked polysilastyrene, crosslinked poly(tetramethyldisilylene-co-styrene) and crosslinked dimethyldichlorosilane have been developed using a chemical crosslinker divinyl benzene. This work will be presented in detail in the section that deals with Results and Discussion.

The selection of silicate matrices is based on fabrication route, utilizing the viscous flow property of the parent glass and the ability to tailor thermal expansion near to that of the fibers. The key to the successful development of silicate matrix composites lies in the fact that it has been carried out as a direct extension of metal and resin matrix composites. In each case, high modulus fibers have been incorporated into a low elastic modulus matrix to achieve structural reinforcement. Glass and glass-ceramic moduli are in the range of 60 to 85 GPa while the reinforcing fibers are generally characterized by an elastic modulus in excess of 210 GPa. These composites are also fabricated in the same manner totally analogous to that used for resin matrix composites. This is due to the fact that a glass matrix can be readily deformed and flowed in its low viscosity state at elevated temperatures. Glass-ceramics provide a great potential for high temperature applications. They also provide a unique capability to densify a composite in the glassy state and then subsequently crystallize the matrix to achieve high temperature stability. Techniques used to fabricate resin matrix composites can be adapted to glass and glass-ceramic matrix composites. The composites which result from the above processing are characterized by high strength, stiffness, toughness and in general the overall performance is similar to that of resin matrix composites except that in this case performance can be maintained up to a temperature as high as 1200°C. In addition, these composites are also not susceptible to environmental degradation due to moisture, oils or fuels. While the fibers at first appear to be the dominant determiners of composite characteristics, it is the matrices and their wide range of compositions and physical properties, which give the material scientist the control necessary to tailor a successful material. The matrix composition not only contributes to composite properties such as elastic modulus, coefficient of thermal expansion and high temperature creep resistance, but more importantly matrix compositions provide a means of controlling the fiber matrix reaction during the composite densification step. The reactivity or lack there of in large measure determines composite fraction mode[4]. The other major advantage is that

glass-ceramics can be prepared by the low temperature sol-gel method. Glass-ceramic matrices offer major advantages in relation to efficiency and performance of gas turbines. Their potential for a high temperature operation reduces the need for cooling and their low density reduces weight and stress created in moving components. The glass-ceramic route has extended the matrix range temperature capability, typically to aluminium compositions such as $Li_2O-Al_2O_3-SiO_2$ (LAS), $MgO-Al_2O_3-SiO_2$ (MAS), $CaO-Al_2O_3-SiO_2$ (CAS) and $BaO-Al_2O_3-SiO_2$ (BAS). Among the various silicate systems, BAS occupies a prominent place due to its ability to crystallize into the highly refractory phase celsian ($BaAl_2Si_2O_8$). Celsian is considered as a possible precursor material for refractory composites due to its high melting temperature and high oxidation resistance. These ceramics have attracted considerable interest for advanced engineering applications due to the unique combination of properties such as high melting temperature, low thermal expansion and low and thermally stable dielectric constant and loss tangent[16]. Celsian exists in two different forms i.e., monoclinic and hexagonal forms. Although the monoclinic form is stable from room temperature to 1590°C, glasses normally crystallize as metastable hexacelsian even below 1590°C[17]. Since monoclinic celsian has a lower thermal expansion coefficient compared to hexacelsian it is preferred in composites. In this study, various methods to stabilize monoclinic celsian have been attempted and an attempt has been made to understand the underlying mechanisms.

In summary, in this study two key problems have been studied. One, the development of an alternate stable precursor for refractory SiC fibers and the other, the stabilization of monoclinic celsian through different chemical additives. Both are important from the view point of ceramic matrix composites (CMC'S) development in India.

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Chapter 2

Literature Review

Section A - Development of Precursors for SiC Fibers

2.1 Introduction

In recent times, methods such as chemical vapour deposition (CVD), sol-gel technology and polymer pyrolysis have been used for the production of high purity ceramic starting materials alongside the classical powder metallurgical processes. Many new technologies have emerged with the use of these methods. In all the three methods, ceramic is produced from low molecular weight, inorganic or organometallic precursors. The latter are molecular species containing direct polar $E^{\delta+}$ - $C^{\delta-}$ bonds between the element E and carbon. E can be a metal or a non-metal, giving these methods greater potential in ceramic production and processing. In contrast to the sol-gel process which is ideally suited to the production of oxide glasses and ceramics, the solid state pyrolysis of inorganic polymers is best suited to the synthesis of non-oxide, non-metallic materials[1-3].

In the pyrolysis of inorganic polymers, ceramic precursors are monomers or polymers, containing all the elements to be present in the final material and can be processed to obtain the final material. The idea behind the approach is to carry out changes at atomic level which in turn will change the properties of the materials. The definition of ceramic precursors is very broad and includes each and every compound known. In principle, it is true that every compound can be converted to materials under the right set of conditions. However, the intent of developing preceramic routes is not to use each and every known compound to prepare materials. There are some requirements on precursors which qualify them as ceramic precursors i.e. the monomer should be readily available and inexpensive, the polymer chemistry should be simple, the polymer should be liquid fusible or soluble in an organic solvent, the polymer should be stable in air at room temperature, the pyrolysis chemistry should proceed smoothly with a high yield and minimum of violent gas evolution and the pyrolysis off gases should be non-hazardous. Additionally, attention should also be paid to some chemical facts. It is important to realise that many long chain linear inorganic polymers self destruct upon pyrolysis by the evolution of small, volatile cyclic units. As a

result, large amount of the precursor building blocks are lost to the gas phase and the ceramic yields are low. In order to overcome this tendency, reactivity centres or crosslinks are built into the polymer. The degree of crosslinking must be carefully varied with consideration of the application for the polymer e.g. fibers, coatings or foams. To prevent incorporation of deleterious impurity elements in the final ceramic, care must be exercised over the elemental and structural composition of the monomer and polymer. In turn, this requires an in-depth knowledge of the thermodynamics and kinetics of inorganic reactions taking place in the formation of the monomer and polymer and occurring in subsequent crosslinking and calcination process steps. The advantage of the preceramic route is that polymer precursors can be converted to shaped article without complex preprocessing and this would alleviate many processing problems[4,5]. In the last 25 years a number of inorganic polymers have been developed. Some of the important polymers and their resulting ceramic products are given in Table 2.1.

Table 2.1 A Partial History of Non-Oxide Ceramics from Polymer Pyrolysis

Inorganic Polymers/Precursors	Resultant Ceramic	Reference
Polycarbosilane	SiC	6–15
Polysilastyrene	SiC	16
Polytitanocarbosilane	Si–Ti–C-O	17
Polyzirconocarbosilane	Si–Zr–C-O	18,19
Polysilazanes	Si–C-N	20 23
Carboranesiloxane	SiC–B_4C	24
[Al–N(H)Si(CH_3)$_3$]$_2$	AlN	25
[(C_4H_9N)$_2$Ti]$_n$	TiN	26
Zr(BH_4)$_4$	ZrB_2	27

2.2 Importance of SiC Ceramic in Engineering Applications

Because of its excellent mechanical strength and chemical stability at high temperature, SiC (Nicalon) is used in various heat-resistant materials. Nicalon fabric has been used as a heat-resistant sealing material (gap filler) for the ceramic tiles on the outside of the space shuttle and as a sealant for the doors there of. General industrial applications include

thermal insulating materials for high temperature furnaces, conveyer belts, high temperature gas and molten metal filters. In addition, because it has the electrical resistance of a semiconductor, Nicalon is used in high voltage cables as an electrostatic coater. Nicalon/plastic composites possess superior mechanical properties and microwave absorption or electrical insulation. As a result, they are used as microwave-absorbent structural materials, heat resistant structural materials and insulating structural materials in aircraft. General industrial applications of this composite include continuous welding machines for seam-welded pipes in steel mills, where they have contributed to the more efficient production of steel pipes[28]. Among the SiC/metal composites, mainly aluminium composites have reached the stage of practical application. Because of their light weight and heat resistance, they are used in aircraft components, equipment and materials for space development, automotive parts, general mechanical components and sporting goods for advanced performance[29]. SiC/ceramic composites are used in thermal shielding and furnace walls of high temperature annealing furnaces, while in tubular form it is used in thermal–impact resistance tubes of high temperature and radiant furnace tubes[30]. In summary, development of applications for SiC–reinforced composites is proceeding in a variety of fields with the aim of improved material performance, and these materials are making significant contributions to the development of advanced technologies.

2.3 SiC and its Structure

SiC exists in two forms, α and β. The α form exists either in a hexagonal or a rhombohedral structure. β has a diamond cubic structure. The cubic form is a low temperature modification (β-SiC) and the hexagonal form is a high temperature modification of SiC (α-SiC). In addition to the common cubic and hexagonal forms, SiC displays periodic stacking faults due to the placement of the additional layer in an alternate arrangement which creates the polytypes[31]. Mclarsen has calculated theoretically the number of possible polytypes for 50 layers to be 93,813,567. In reality the number of polytypes observed are approximately 200. Several notations are used to describe the polytypes of silicon carbide, the most common being the Ramsdell notation. The Ramsdell notation has two parts, the first number describes the number of layers in one unit cell and the second letter indicates the type of lattice structure. Some of the important polytypes are

2H, 6H, 15R and 3C. 3C form is generally known as β-SiC and the other polytypes are referred to as α-SiC.

2.4 Conventional Processing Routes for SiC

2.4.1 From SiO₂

SiC can be prepared by heating any source of carbon and silicon at a high temperature. Commercially, SiC is prepared by the Acheson's process. The conversion of SiO_2 (quartz sand or crushed quartz) takes place by the following reaction. Here the source of carbon is anthracite coal or petroleum coke.

$$SiO_2 + 3C \longrightarrow SiC$$
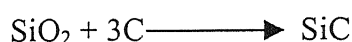
2.4.2 From Silicon

Elemental silicon in solid, liquid or gas phase forms SiC on reaction with carbon

$$Si_{s,l,g} + C \longrightarrow SiC$$
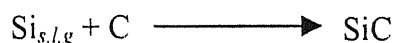
The reaction temperature is in the range of 900°C–1500°C and depends on the phase of silicon and carbon[4].

2.4.3 From Silicon Tetrachloride

Silicon tetrachloride is another inexpensive reagent which is used as a source of silicon for the preparation of silicon carbide. Since silicon tetrachloride is a low boiling liquid, it can be introduced into the reaction vessel as gas. Hydrogen gas is required for all the reactions to remove chlorine and excess carbon[32].

$$SiCl_4 + C \xrightarrow{1300°C-1500°C} SiC$$

$$SiCl_4 + CH_4 \xrightarrow{1300°C} SiC$$

$$SiCl_4 + C_3H_8 \xrightarrow{1200°C} SiC$$

$$SiCl_4 + C_6H_6 \xrightarrow{1700°C-1800°C} SiC$$

$$SiCl_4 + C_6H_5CH_3 \xrightarrow{1600°C-1900°C} SiC$$
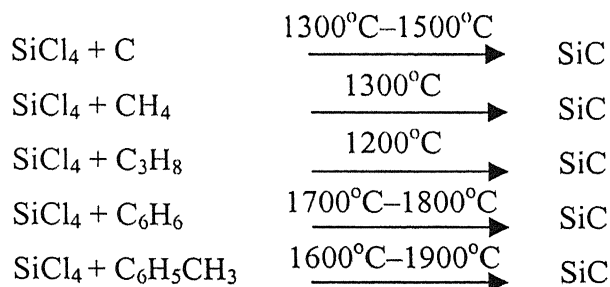
SiC is a covalent solid where diffusion is slow and so it is difficult to sinter. It is also difficult to obtain SiC in the fiber or film form by normal inorganic chemical processes. SiC

fibers are at present produced by either chemical vapour deposition or polymer precursor method. The concept for the synthesis of SiC fibers by polymer precursor method can be readily seen from the synthesis of carbon fibers, which are used in carbon fiber reinforced materials. Carbon fibers are produced in a large scale from polyacrylonitrile (PAN)[33]. In the carbon fiber preparation process, the skeleton remained after pyrolysis is made up of carbon. To obtain a skeleton composed of Si and C, the heating of an organometallic polymer can be used. The main advantage of this polymer precursor method is that organometallic precursors can be spinned in the form of fibers. In this way, it is possible to obtain ceramic in forms impossible to achieve by traditional inorganic chemical processes. This processing method also eliminates the use of sintering additives in forming the complex bodies due to good sinterability of the fine pyrolized powder[34].

2.5 General Outline for obtaining SiC from Organic Precursors

The various steps involved in the synthesis of SiC from polymer precursor is given below[35]. Each step will be discussed in detail in the following sections.
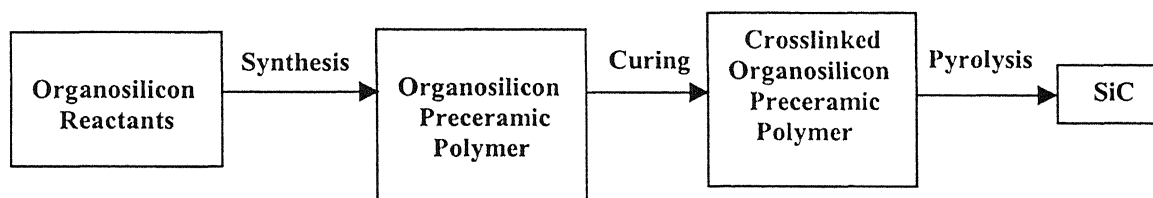
2.6 Different Routes for the Preparation of Polymer Precursors

Polysilanes[36-38] and polycarbosilanes[6-15] have been extensively studied as precursors for the preparation of silicon carbide. Polysilanes are polymers with a silicon backbone and polycarbosilanes are polymers containing alternate Si and C atoms in the backbone. In principle, all known polysilanes and polycarbosilanes could furnish silicon carbide. The stability of polysilane and polycarbosilane as precursors depends on the ease of synthesis in pure form, processing condition and purity of silicon carbide. The first polysilane $(Ph_2Si)_n$ was probably prepared by Kipping et al.[36-38] in their search for Si=Si bonded species. Burchard[39] prepared $(Me_2Si)_n$ in the late forties and found that this material was insoluble, infusible and intractable. Since then a large number of polyorganosilanes have been prepared which are soluble and fusible[6-15].

2.6.1 Polycarbosilane

Polycarbosilane is a general term for organosilicon polymers with alternate Si and C atoms in the backbone. Many kinds of polycarbosilanes have been synthesized using various methods. Polycarbosilanes are usually synthesized by thermal decomposition of monosilanes or disilanes and by the ring opening polymerization of disilacyclobutanes. The different polycarbosilane prepared by different methods are listed below.

PC-TMS

The polycarbosilane (PC-TMS) was prepared by heat condensation of tetramethylsilane at 700°C, circulating unreacted silane in a continuous pyrolysis furnace[40-42].

PC-D

From dodecamethylcyclohexasilane (DMCHS), a polycarbosilane (PC-D) was obtained. Dimethyldichlorosilane was converted to DMCHS by addition of lithium chip or wire in tetrahydrofuran solvent. The DMCHS was ring cleaved and polymerized in an autoclave at about 400°C to yield PC-D[43,44,7]. This method, however, is technically difficult, expensive and time consuming because of the use of lithium metal and a low conversion yield of DMCHS to PC-D.

PC-A

In an alternative route, a polycarbosilane (PC-A) was obtained from polydimethylsilane (PDS). In the first step, dimethyldichlorosilane was subjected to dechlorination condensation in xylene, and these were heated under nitrogen gas to produce PDS powder. The PDS was then heated at 450°C–470°C under an argon atmosphere in an autoclave to give PC-A[41,42,45]. This process is considered to be technically difficult and expensive because of the need to use an autoclave.

PC-N

The earlier PDS was pyrolyzed and polymerized under N_2 gas flow at normal pressure (without an autoclave) using reflux condenser and a polycarbosilane (PC-N) was obtained with a yield of about 50%. It is now produced in an industrial scale[46].

PC-B

When pyrolyzing PDS under normal pressure, a few percent of polyborodiphenylsiloxane (PBDPSO) can be added so that the reaction then proceeds by a catalytic enhancement of the rate. Table 2.2 shows the yields of various polycarbosilane obtained under various

synthetic condition[11,42,47,48]. Fig. 2.1 summarizes the chemical reactions for the syntheses described in the above sections.

Table 2.2 Synthesis Condition, Yield and Number Average Molecular Weight of Polycarbosilanes.

Polycarbosilane	Temperature (^{o}C)	Time (hour)	Distillation temp/pressure (^{o}C / torr)	Yield (%)	Molecular weight ($\overline{M}_n$)
PC-N-470	470	120	280/1	50 – 55	1500
PC-A-470	470	14	280/1	58.8	1680
PC-B-3.2	350	10	280/1	50	1740
PC-B-5.5	350	10	320/760	64.8	1310
PC-TMS	760	27	200/1	6.5	620
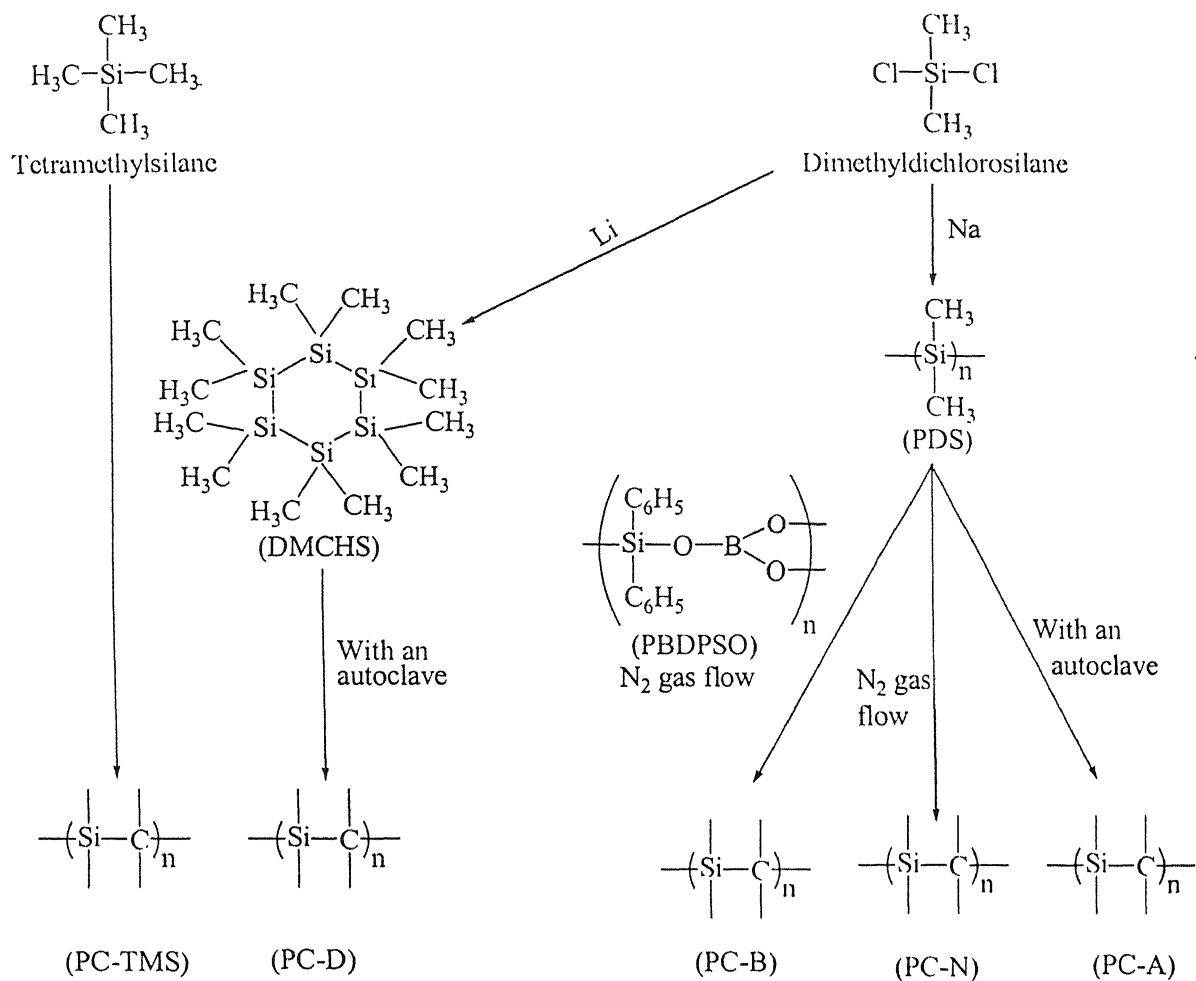
Fig 2.1:The preparation of ceramic fibers obtained from various polycarbosilane[6].

13

2.6.2 Phenylmethylsilane–Dimethylsilane Copolymers as Precursors to Silicon Carbide.

The dechlorination of a mixture of dichloromethylphenylsilane with sodium/potassium alloy in boiling toluene results in the copolymer with the IUPAC name catena - Poly[(dimethylsilicon) (phenyl methyl silicon)] with the idealized formula as shown below:

$$x \ Me_2SiCl_2 + y \ Me(Ph)SiCl_2 \longrightarrow 1/n \ [(Me_2Si)_x(Me(Ph)Si)_y]_n + 2 \ (x+y) \ NaCl/KCl$$
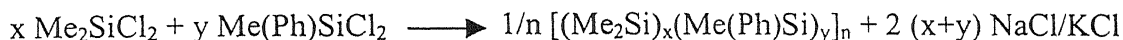
where Me stands for methyl and Ph for phenyl group. The advantage of this method is that in this method the conversion of the copolymer to SiC occurs without the need for intermediate tempering in an autoclave. This is in contrast to pure poly(dimethyl)-silane which has to be converted first into polycarbosilane at $450^{\circ}C$ and a pressure of 10 MPa before pyrolysis to form SiC[16,49].

2.6.3 Polysilethenesilethyne - A Promising Precursor to Silicon Carbide

A new polymer polysilethenesilethyne, was prepared through the reaction of dimethyl bis (bromo magnesium ethynyl) silane with E,E–bis(2–dimethylchlorosilylvinyl) dimethylsilane by Yarosh and co-workers[50].
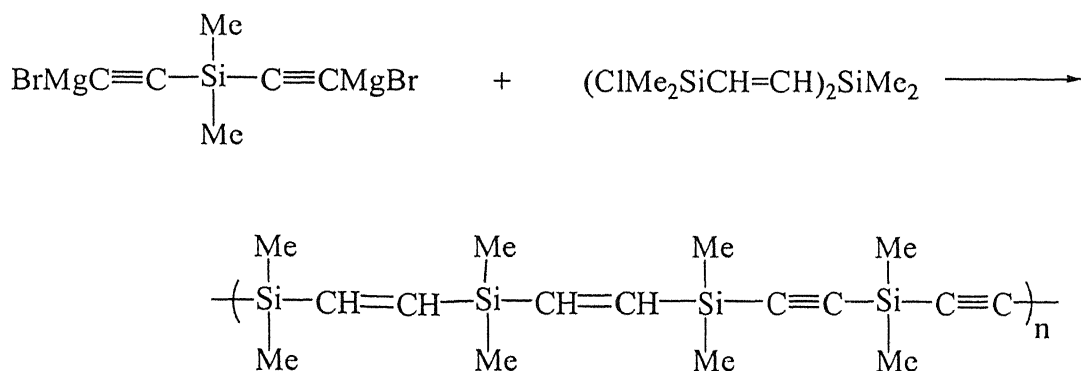
where Me is the methyl group. From the mixture of products, by high vaccum distillation, low molecular weight products were removed and the resulting product is a yellow white solid. Advantage of using this polymer as the precursor is the simplicity and technological efficiency of the precursors obtained and the presence of double and triple bonds which can be helpful in crosslinking process and high ceramic yield[51,52]. However the future use of this precursor is limited due to decomposition and crystallization of the ceramic product.

2.6.4 Chlorine Containing Polycarbosilane as Precursors for Nanocrystalline Silicon Carbide Powder

The chlorine containing polysilane (PS) or polycarbosilane (PCS) was synthesized by the catalytic redistribution of bis(chloromethylsilane) to yield monosilanes and poly (chloromethylsilane) by oligomers[53 55]. The oligomers were converted to poly (chloromethylsilane) by thermally inducing crosslinking reactions, increasing the molecular weight of the molecules and simultaneously cleaving trichloromethylsilane(monosilane). Styrene was added to the reaction mixture in the redistribution reaction, yielding a copolymer with improved spinning properties. Stoichiometric SiC can be obtained as a consequence of the chlorine content in poly(chloromethylsilane), which allows an adjustment of the carbon content of the precursor molecules in contrast with the silicon polymers with alkyl and aryl groups[56,57]. The nanocrystalline morphology of the grains and the structure of the interfacial grain boundaries should improve the mechanical properties of the SiC particulate reinforced composites[58].

2.6.5 Polytitanocarbosilane–A Promising Precursor to Si–Ti–C–O Ceramic

Polytitanocarbosilane (PTC) is synthesized by heating a mixture of polydimethylsilane and polyborodiphenyl-siloxane with titanium alkoxide at about 340°C in nitrogen gas to affect polymerization[17,59]. During the process, the cleavage of the Si–Si bonds in polydimethylsilane, the formation of Si–H and Si–CH$_2$-Si bonds , the condensation of Si–H bonds and crosslinking by the titanium compound occurs simultaneously with polyborodiphenylsiloxane serving as the catalyst[60].

2.6.6 Polyzirconocarbosilane–A Promising Precursor To Si–Zr–C–O Ceramic

This polymer was prepared by mixing polycarbosilane with zirconium n-butoxide, $Zr(OBu^n)_4.Bu^nOH$ in toluene. The molar ratio of Zr/Si is 25%. A crosslinked polymer was formed by heat–treatment up to 300°C when polymer became no longer fusible[18]. Polyzirconocarbosilane can also be produced by reaction of polycarbosilane with zirconium(IV)acetyl acetonate at 573 K in nitrogen atmosphere. The reaction occurs by condensation reaction of the Si-H bonds in polycarbosilane and the ligands of zirconium(IV)acetylacetonate and it is accompanied by the evolution of acetyl acetone. The molecular weight increases by crosslinking reaction with the formation of Si–Zr bond[19].

2.6.7 Chemically Modified Polycarbosilane as a Precursor to SiC

Chemically modified polycarbosilane containing organofluoric groups (PCOCF) was synthesized to improve the abilities of handling and compaction behaviour of SiC powders. Synthesis consisted of three steps. First step involved the synthesis of polycarbosilanechloride (PCCl), in which active chlorines are added to side chains of polycarbosilane. Second step consisted of preparation of sodium fluoric alkoxide ($NaOCH_2CF_2CF_3$). The final step was the reaction of PCCl with $NaOCH_2CF_2CF_3$ resulting in the formation of chemically modified polycarbosilane. The yield of SiC from PCOCF was improved compared with unmodified PC due to the increased molecular weight of the precursor[61]

2.6.8 Other Processing Methods

Another important precursor poly(silaethylene) can be prepared by the ring opening polymerization of 1,3-disilacyclobutane catalyzed by H_2PtCl_6. For the synthesis of another precursor poly(silapropylene), 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane is mixed with chloroplatinic acid and heated to 80°C. The resulting polymer is reduced by treatment with lithium aluminium hydride resulting in the formation of polysilapropylene[62]. Hydrosilylation reactions of vinyldichlorosilanes have been investigated by Corriu as means to prepare polycarbosilanes. Hydrosilylation is accomplished in the presence of Pt/C catalyst and the resulting polymer is reduced by $LiAlH_4$, $HSiCl_3$ or $(CH_2=CH_2)_2SiCl_2$ can also be added to vinylchlorosilane. The molecular weights of the polymers are dependent on

the solvent used during polymerization[63]. Laine et al.[64] have prepared polymers by the dehydrocoupling of silanes. The commonly used monomer is methylsilane although ethyl and vinyl silanes have also been used. Several catalysts have been found to be useful for the polymerization and most effective catalysts are Cp_2TiMe_2, Cp_2ZrMe_2 or Cp_2HfMe_2.

The polymer obtained is spun into fibers by a melt spinning method. At this stage fibers are very fragile because they are not crosslinked. Crosslinking of the polymer to make it infusible is called as curing. There are different methods of curing like oxidative curing, electron/neutron irradiation curing, photocrosslinking and chemical crosslinking. Curing is necessary to permit the conversion of polymers into the ceramic without softening during the process[65].

2.7 Curing and Pyrolysis

2.7.1 Curing by Oxidation

Curing by oxidation is achieved by crosslinking the polycarbosilane with oxygen. It is presumed that the curing mechanism results in the formation of Si–O–Si or Si–O–C bonds by the oxidation of Si–H and Si–CH$_3$ in the polycarbosilane. In the synthesis of silicon carbide fiber, polycarbosilane fibers were cured by heating in air. It was found that the weight gain of PC-470 and PC-TMS by curing are about 7.5% and 2.3%, respectively. The fibers were found to be infusible and the conversion process of polycarbosilane to SiC is affected. From the TG–DTA curves it is clear that by curing, the weight losses of PC-470 and PC–TMS in the first stage is reduced and the curing process hardly affects the weight losses in the second and third stages of both the fibers[41] (Fig. 2.4(a), Fig. 2.4(b)). The fibers are oxidatively cured at 190°C in air to crosslink polycarbosilane molecules. Depending on the curing conditions properties of SiC fibers vary. Using various techniques such as IR spectroscopy, UV spectroscopy, X-ray analysis, Raman spectroscopy, Magic angle spinning-Nuclear magnetic resonance (MAS–NMR) spectroscopy etc, six steps are identified in the conversion of polycarbosilane to SiC fiber[66 69].

(i)   The weight loss due to the evaporation of low molecular weight components and increment in molecular weight.

(ii)   Molecular weight increases by dehydrogenation and dehydrocarbonation condensation.

(iii) Side chain decomposition by dehydrogenation and demethanation and the inorganic structure starting with formation of Si–C and C- C bonds.

(iv) Formation of amorphous SiC.

(v) Formation of β-SiC with further dehydrogenation, the product containing excess carbon and silica.

(vi) Crystal growth of crystalline β-SiC with a decrease in Si-O bonds due to the reaction with excess carbon.

In PCS, a transition from amorphous to crystalline form occurs approximately at 1000°C although the crystallization becomes clearly visible at 1200°C. Beyond 1200°C, free carbon dispersed in the fiber reacts with oxygen and forms CO. Following various progressive readjustments, the fiber gains strength till 1200°C and beyond that the strength decreases drastically due to evolution of CO[51,70]

2.7.2 Electron/Neutron Irradiation Curing

At high temperatures the tensile strength of SiC fibers decrease rapidly due to the CO gas evolution. In order to improve the high temperature property of SiC, an oxygen free curing process was studied. Electron irradiation increased the density and mechanical properties of the fiber[35,71] . The curing mechanism during irradiation process was found to be breakage of Si–H and C–H bonds and formation of Si–C, Si–Si bonds. The pyrolytic reaction from PCS to SiC proceeds through free radical mechanism. There are two steps in the major reaction. The radicals are formed on the Si atoms by Si–H cleavage in the intial stage at 800–1000 K and are formed on the C atoms by C–H cleavage in the PCS chain in the second stage at 1000–1800 K. Radical concentration reflects the rate difference between formation by cleavage of Si–H and C–H bond and the decay by the recombination of the radicals. In the intial stage, the Si central radical concentration decreases with an increase of the oxygen content in the cured PCS fibers because of decrease of Si–H content by the oxidation in Si–H. The ESR spectrum and radical concentration are characterized by the state of pyrolysis. An understanding of these reaction mechanisms and the reaction kinetics would be very useful in controlling the pyrolysis process to obtain improved SiC fibers[72,73].Commercially these polymers are referred to as Hi–Nicalon.

18
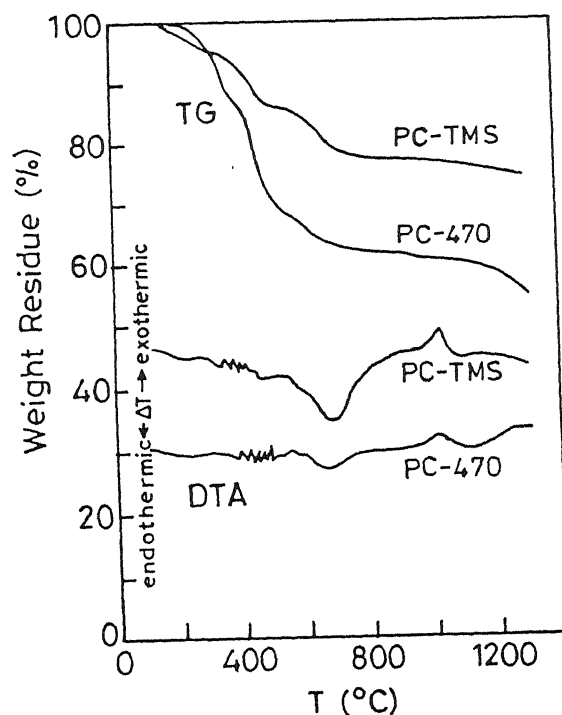
Fig 2.2 (a): TG – DTA curves of PC – 470 and PC – TMS in an N_2 flow[41]
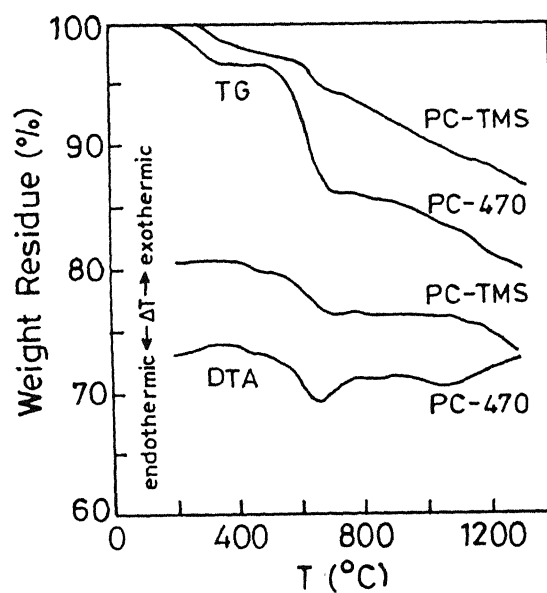
Fig 2.2 (b): TG – DTA curves of cured PC – 470 and PC – TMS in an N_2 flow[41]

2.7.3 Photocrosslinking

Crosslinking can also be done by using ultraviolet rays–called as photocrosslinking. Polysilastyrene, a precursor for SiC was crosslinked by UV light. Polysilastyrene shows a strong UV absorbtion at 330 nm. The polymer is also photoreactive. When solutions of polysilastyrene are exposed briefly to UV light or even for long periods to room light the molecular weight decreases. In the solid phase photolysis of the polymer with UV light of wavelength 350 nm or less transforms it into a more rigid, less soluble form with higher modulus and greater elastic recovery indicating crosslinking in the polymer. The crosslinking is important in further processing to silicon carbide because the crosslinked polymer will retain its shape during firing. Polysilastyrene loses 70% of its weight upon heating under nitrogen at 10^oC / min rise in temperature upto 800^oC.

$$(PhSi_2Me_3) \longrightarrow Ph\,H + CH_4 + 2H_2 + 2SiC$$
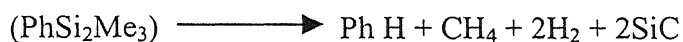
Polysilastyrene was then tested as precursor for forming silicon carbide fibers. It was found that crosslinked polysilastyrene can be fired to form β-SiC while retaining its physical shape[16].

2.7.4 Chemical Crosslinking

Crosslinking can also be done using chemicals. For example, polycarbosilane can be crosslinked using polybutadiene. Polydimethylsilaethylene was prepared from 1,1,3,3–tetramethylcyclobutane and was chlorinated with Me_3SiCl in the presence of $AlCl_3$. The polymer is crosslinked by reacting with Na, K, $MeNH_2$, NH_3, H_2O or 1,3–butadiene[74,75].

2.7.5 Silicon Carbide By Laser Pyrolysis of Polycarbosilane

Conventional pyrolysis of PCS to form fibers involves melt spinning, curing and then pyrolysis. The laser pyrolysis process differs significantly from conventional pyrolysis since it is a single step process. PCS is directly pyrolyzed by scanning laser in flowing argon. Like the electron beam curing method, polymer solution techniques and chemical vapour curing, laser pyrolysis does not introduce oxygen during processing. Avoiding oxygen is beneficial because oxygen reduces the high temperature strength of silicon carbide. Laser pyrolysis of polycarbosilane produces controlled three dimensional shapes of β-SiC.

Shrinkage, porosity and cracking remain serious problems, but the use of fillers shows promise in reducing these problems[76].

2.8 Properties of SiC fibers

The performance of a ceramic matrix composite (CMC) is highly dependent upon the properties of the reinforcement. A reinforcing fiber should have high environmental stability and sufficient mechanical properties even at high temperature. SiC fibers, which have high tensile strength, high elastic modulus and good thermal stability are one of the best candidates for reinforcement. SiC fibers produced via polymer pyrolysis have an advantage of flexible, fine diameter over those from chemical vapour deposition or sintering process[9]. One highly commercialized polymer-derived SiC fiber, Nicalon, has been widely applied in many high temperature structural materials[77,78]. Recently, the SiC fiber with a low oxygen content, Hi-Nicalon has been developed. This fiber has a higher elastic modulus and creep resistance and much improved thermal stability over that of Nicalon fiber[79-82]. Hi-Nicalon has permitted production of ceramic matrix composites with improved mechanical properties. However, Hi-Nicalon mainly consists of SiC microcrystals and amorphous carbon. The fiber with relatively smaller crystallites would cause creep deformation more easily at high temperature and excess carbon in fiber would not have a favourable influence, especially with regard to oxidation resistance. Therefore, a SiC fiber with stoichiometric composition and high crystallinity was desired for making composites with further improvement in properties. The near stoichiometric, highly crystalline SiC fiber named Hi-Nicalon type S has been developed[83]. The properties of all the PCS derived fibers are compared in Table 2.3. Nicalon fiber exhibited low strength after 1400°C, no strength after exposure at 1500°C. Hi-Nicalon and Hi-Nicalon type S retained good strength even after 1600°C exposure. Hi-Nicalon type S showed the highest strength, 1.8 GPa, after 10 hours exposure in argon at 1600°C. Hi-Nicalon type S showed the best oxidation resistance on strength basis. Hi-Nicalon type S exhibits improved creep resistance over Nicalon and Hi-Nicalon due to larger crystalline size[84].

Table 2.3 Typical Properties of PCS Derived SiC Fibers

Properties	Nicalon	Hi-Nicalon	Hi–Nicalon type S
Fiber diameter (μm)	14	14	12
Number of Filaments(fil/yarn)	500	500	500
Tensile Strength (GPa)	3.0	2.8	2.6
Tensile Modulus (GPa)	220	270	420
Elongation (%)	1.4	1.0	0.6
Density (g/cm^3)	2.55	2.74	3.10
Specific Resistivity (Ohm–cm)	$10^3 - 10^4$	1.4	0.1
Chemical composition Si	56.6	62.4	68.9
C	31.7	37.1	30.9
O	11.7	0.5	0.2
C / Si (atomic)	1.31	1.39	1.05

Section B: Stabilization of Monoclinic Celsian

2.9 Introduction

Nearly all ceramic materials are potential matrix materials depending upon the application foreseen for the composites. Important attributes for matrix selection are refractoriness, compatibility with fibers and composite fabricability. Potential matrices include glass and glass-ceramics, crystalline oxides, carbides, borides and nitrides. Glass and glass-ceramics have been widely used owing to their relative ease of composite fabrication by hot pressing[85]. Glass and glass-ceramic matrices have been reinforced with high modulus graphite fibers[86,87], silicon carbide fibers and silicon carbide monofilaments[88,89]. Several fold improvement in strength and fracture toughness of glass and glass-ceramics has been obtained ·by reinforcing these matrices with silicon carbide whiskers. Incorporation of whiskers in the matrices results in a tremendous increase in viscosity, thus necessiating much higher composite processing temperature compared to that of the matrix alone[90]. The use of glasses to achieve high temperature composites was, however, difficult due to higher temperatures required to densify the composites during hot pressing. Through the use of glass-ceramic matrices this difficulty was overcome since these compositions could be hot pressed in a low viscosity state and then crystallized to achieve a high temperature composite[85]. Glass-ceramics offer a very broad range of matrix chemistries that can be tailored to the particular fiber reinforcement available. The glass and glass-ceramics which are used as the matrix type are listed in Table 2.4. The advantages of silicate matrices in composites stem from their relatively low temperature fabrication, the varied glass chemistry and the possibility of post fabrication crystallization to a variety of silicate phases with tailored thermal expansion. The residual stress due to thermal expansion mismatch and a low cohesion fiber/matrix interface are two important parameters to be considered in the development of ceramic matrix composites. The former viz., thermal expansion of the matrix is tailored to match that of the fiber, by controlling composition, processing and the post fabrication treatment. The compositions of various glass-ceramic matrices in Table 2.4 have been tailored to achieve optimization of composite strength, toughness and environmental stability. The composites of LAS 1, 2, 3 (Table 2.4) and BMAS matrices with SiC yarn are capable of achieving use temperature from 1000°C to over 1250°C. The

ternary mullite and the hexacelsian glass-ceramic matrices have potential composite use temperature of $1500^{\circ}C$ to $1700^{\circ}C$. The ability to achieve high levels of composite crack growth resistance is probably the most significant feature distinguishing high strength fiber reinforced glass-ceramics from unreinforced ceramics. Among the various silicate systems, barium aluminium silicate (BAS) occupies a prominent place due to the reason as given in Chapter1. In composites, monoclinic celsian is preferred over metastable hexacelsian due to its lower thermal expansion mismatch and hexacelsian undergoing a reversible transformation from orthorhombic to hexagonal celsian with accompanying thermal expansion (approximately 4%)[91]. The main characteristics of barium aluminosilicate system are highlighted in the following sections.

Table 2.4 Glass Ceramic Matrices of Interest[92]

Matrix type	Major constituent	Minor constituent	Major crystalline phase	Maximum temperature composite form($^{\circ}C$)
LAS-1	Li_2O, Al_2O_3, MgO, SiO_2	ZnO, ZrO_2, BaO	β-Spondumene	$1000^{\circ}C$
LAS-2	Li_2O, Al_2O_3, MgO, SiO_2, Nb_2O_5	ZnO, ZrO_2, BaO	β-Spondumene	$1100^{\circ}C$
LAS-3	Li_2O, Al_2O_3, MgO, SiO_2, Nb_2O_5	ZrO_2	β-Spondumene	$1200^{\circ}C$
MAS	MgO, Al_2O_3, SiO_2	BaO	Corderite	$1200^{\circ}C$
BMAS	BaO, MgO, Al_2O_3, SiO_2	-	Barium Osumullite	$1250^{\circ}C$
Ternary mullite	BaO, Al_2O_3, SiO_2	-	Mullite	$1500^{\circ}C$

LAS - Lithium aluminium silicate
MAS - Magnesium aluminium silicate.
BMAS - Barium aluminium magnesium silicate.
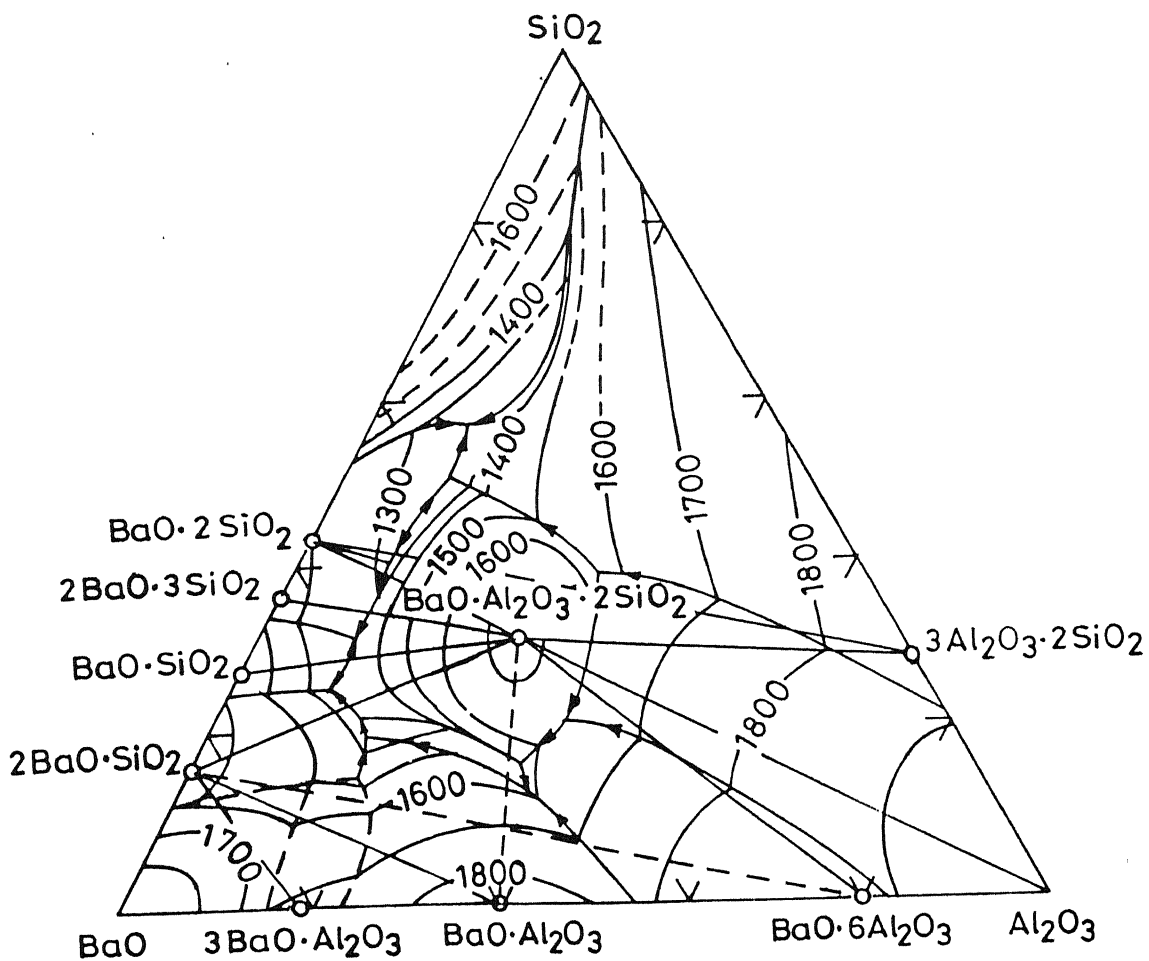
Fig. 2.3: Phase diagram for BaO-Al$_2$O$_3$-SiO$_2$ system[93]

2.10 Phase Diagram of BaO-Al$_2$O$_3$-SiO$_2$

The phase diagram of BaO-Al$_2$O$_3$-SiO$_2$ is shown in Fig. 2.3. In the study of the ternary diagram, 305 compositions were synthesized and subjected to test. The whole diagram (Fig.2.3) comprises of 13 phases of stability. They are: Tridymite (SiO$_2$), Mullite (3Al$_2$O$_3$.2SiO$_2$), Corundum (Al$_2$O$_3$), Barium hexa aluminate (BaO.6Al$_2$O$_3$), Barium mono aluminate (BaO.Al$_2$O$_3$), Tribarium aluminate (3BaO.Al$_2$O$_3$), Barium Oxide (BaO), Dibarium silicate (BaO.2SiO$_2$), Monobarium silicate (BaO.SiO$_2$), Ternary solid solution (2BaO.3SiO$_2$-BaO.2SiO$_2$-BaO.Al$_2$O$_3$.2SiO$_2$), Barium disilicate (BaO.2SiO$_2$), Celsian (BaO.Al$_2$O$_3$.2SiO$_2$), Solid solution of an incongruent composition (3BaO.3Al$_2$O$_3$.2SiO$_2$). As seen from the diagram, the system consists of two series of solid solutions, one that is ternary and therefore is a rarity among silicate systems. On the diagram (Fig. 2.3) there are three important binary systems. They are celsian-corundum, celsian-dibarium and celsian-monobarium silicate. The fields of crystallization form 24 boundary curves. There are 11 boundary eutectic points and 13 invariant points of which 4 are eutectic and 9 reaction points[94]. Celsian is the only ternary compound observed in the portion of the diagram that was investigated. It distinguished itself by being the only crystalline phase encountered that is monoclinic. Relatively large crystals of celsian form readily from melts high in BaO content but their formation becomes increasingly difficult in compositions with increasing SiO$_2$ content[95].

2.11 Polymorphism of Celsian (BaAl$_2$Si$_2$O$_8$)

Celsian exhibits polymorphism and it exists in three different forms. They are hexacelsian, monoclinic celsian and paracelsian. The hypothetical phase diagram for celsian system is shown in Fig. 2.4. The crystallographic data for all the three forms of celsian is presented in Table 2.5.

Fig. 2.4: Hypothetical phase diagram for celsian system[96]. Cn= Monoclinic celsian Hex = β - hexacelsian, Ortho = Orthorhombic α - hexacelsian, Para = Paracelsian, Liq = liquid

Table 2.5 Crystallographic Data for Celsian System

Polymorph	Crystal system	Space Group	a (A°)	b (A°)	c (A°)	α (°)	β (°)	γ (°)
Monoclinic Celsian [97-99]	Monoclinic	12/c C 2/m	8.627 8.641	13.045 13.047	14.408 7.203	90 90	115.2 115.1	90 90
Paracelsian [100,101]	Monoclinic (Pseudo orthorhombic)	P2₁/a	9.076	9.583	8.578	90	90.21	90
Hexacelsian [102,103]	β-Hexagonal	P6/mmm	5.313	5.313	7.805	90	90	120
	α-Orthorhombic (Pseudo hexagonal)	P6₃/mcm	5.293	9.168	15.58	90	90	90

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		C 2/m	8.641	13.047	7.203	90	115.1	90
Paracelsian [100,101]	Monoclinic (Pseudo orthorhombic)	P2$_1$/a	9.076	9.583	8.578	90	90.21	90
Hexacelsian [102,103]	β-Hexagonal	P6/mmm	5.313	5.313	7.805	90	90	120
	α-Orthorhombic (Pseudo hexagonal)	P6$_{3/mcm}$	5.293	9.168	15.58	90	90	90

2.11.1 Hexacelsian

β-Hexacelsian is stable from 1590°C to the melting point of 1760°C. Although hexacelsian is a high temperature form, it readily crystallizes at room temperature in barium aluminosilicate glasses even below 1590°C[96,104]. β-Hexacelsian is metastable. On cooling to about 300°C, it transforms to another metastable orthorhombic form (α-hexacelsian). This transformation is accompanied by a detrimental ≥0.3 dilatational volume change. This is comparable to that of α to β transition in quartz. Such volume change on the transformation point is a significant property which must be kept in mind for different high temperature applications[103,105]. The β to α hexacelsian transition is not always detected either in mineral or synthetic samples suggesting that β-hexacelsian can be stabilized at room temperature by compositional or microstructural features. The basic units in the crystal structure of hexacelsian consists of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra. In hexacelsian, the tetrahedra form two dimensional hexagonal sheets where all the corners are shared and charge balance is maintained by the presence of Ba^{2+} ions between the adjacent sheets. A schematic structure of hexacelsian is shown in Fig. 2.5 (a). Techniques which have been used for the synthesis of celsian such as crystallization from a melt, solid state reactions, hydrothermal treatments and sol-gel processing result in the formation of hexacelsian as the first product[106].

2.11.2 Monoclinic Celsian

Phase diagram shows that it is a thermodynamically stable polymorph from room temperature to 1590°C[104]. The basic units in the crystal structure consists of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra. The monoclinic structure consists of corner sharing silica tetrahedra which form a three dimensional network and the charge neutrality is maintained by the presence of Ba^{2+} ions in large interstitial sites[106]. However, it is difficult to obtain monoclinic celsian without any stabilizing agents. Addition of mineralizers or monoclinic seed particles have been reported in literature to be necessary to obtain monoclinic celsian[107,108]. A schematic structure of monoclinic celsian is shown in Fig. 2.5(b)
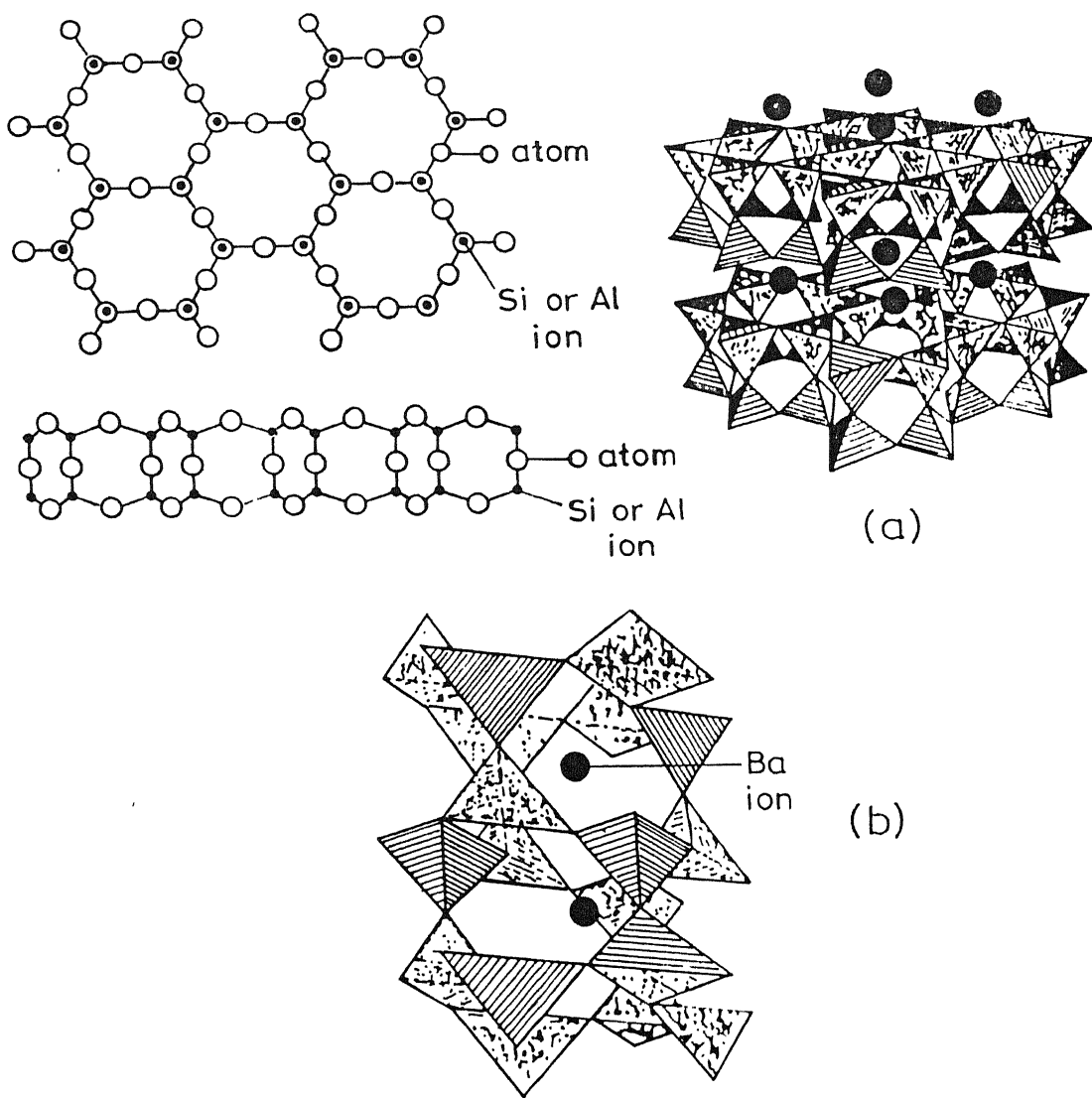
Fig. 2.5: Structure of (a) Hexacelsian; top and middle schematics are plane and elevated views, respectively. Open and black circles represent O atoms and Si or Al ions, respectively, and (b) Monoclinic celsian. The polyhedra represent $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra and Ba ions are represented by black spheres[105]

2.11.3 Paracelsian

Paracelsian is another polymorph of barium aluminosilicate which occurs naturally but can be synthesized only in hydrothermal conditions. The crystal structure of paracelsian is also monoclinic. However, it is commonly referred to as pseudo orthorhombic because all the unit cell angles are approximately 90° in contrast to celsian which has angle β about 115°. The bonding in this structure allows the individual tetrahedra more freedom to tilt and rotate relative to each other compared to that in celsian. Heat treatment of paracelsian above 900°C yields celsian[110].

2.12 Phase Transformations in Celsian System

2.12.1 Low Temperature Transformation (β to α Hexacelsian Transition)

β-Hexacelsian is metastable on cooling to about 300°C when it transforms to another metastable possibly orthorhombic form of α-hexacelsian[104]. The powder diffraction pattern of α and β hexacelsian showed no significant difference except peak shifts owing to lattice expansion indicating that the fundamental frameworks of both the structures are same and it is expected that the change of the structure is confined to slight shift of light atoms[103,106].

2.12.2 High Temperature Transformation (Hexacelsian to Monoclinic)

Although monoclinic phase is the thermodynamically stable phase at temperature below 1590°C, hexacelsian is the first product of crystallization and hexagonal to monoclinic transformation is very sluggish[106]. The experimental results obtained by Lin and Foster[96] and Bahat[108] give us the evidence for this transformation. The sluggish hexagonal to monoclinic transformation could be accelerated through decreasing the particle size of the starting hexacelsian and adding celsian crystalline seeds[104]. For example, the monoclinic celsian can be stabilized in the melt or sol-gel glass-ceramics by adding celsian seed crystals to the glass frit[111] or to the sol prior to gelation and densification[112], by adding mineralizers such as Li_2O to the melt[109] or as lithium isopropoxide to the sol[111], by cold isostatically pressing glass powder followed by heat treatment[111], by moving the sol-gel composition towards $BaO.2SiO_2$ in the ternary $BaO-Al_2O_3-SiO_2$ diagram[92] or by forming a solid solution with $SrAl_2Si_2O_8$[113]. Bahat[114] has investigated the kinetics of hexagonal to monoclinic transformation. The activation energy of crystal growth of celsian from

hexacelsian was found to be quite low (20.1±20 Kcal/mol) suggesting that the transformation does not involve the breaking of Si-O and Al-O bonds. The solid solubilities of silica in the hexagonal and monoclinic modifications of celsian are about 4 and 2% weight, respectively. During transformation of hexacelsian into monoclinic form, excess silica must precipitate out. The transformation of hexacelsian into the monoclinic modification is very sluggish, probably due to the slow rate of diffusion of silica.

2.13 Processing Methods for Celsian

Both celsians have been synthesized by a variety of methods. From amorphous precursors produced by quenching molten oxides, sol-gel processing, ion exchange of zeolites, hydrothermal processing and firing of solid state mixtures[115]. Some of the important methods for processing are discussed below:

2.13.1 Methods for Hexacelsian

Sol–gel Method

Two sol-gel method have been used to prepare hexacelsian $(BaAl_2Si_2O_8)$. In the first method[116], a partial alkoxide route was used. Tetraethylorthosilicate (TEOS) was prehydrated with water with a TEOS/H_2O molar ratio of 1:2 for one hour. In the meantime, aluminium-sec-butoxide was poured into 2-propanol in a volume ratio of 1:3 and a saturated aqueous solution of barium acetate was made. TEOS was mixed with aluminium-sec-butoxide first, followed by addition of barium acetate. After stirring overnight, a jellylike gel was formed within one day in an oven kept at 80°C, and fine powders resulted upon further heating at 110°C for two days. X-ray amorphous xerogel was prepared by heating the powder at 600°C for one day, followed by one day at 800°C. Second method to prepare precursor is an all alkoxide route. Barium metal (0.15 mol) was dissolved in 2-propanol and mixed with 0.3 mol aluminium secondary butoxide at the boiling point and refluxed. Finally, 1.2 mol water and 5 ml 0.01M dilute HCl aqueous solution were added to produce the gel which was dried in an oven at 60°C and then at 80°C followed by calcination at 600°C to obtain zerogel. The gel when examined by X-ray was found to be totally amorphous. It was found that pure hexacelsian crystallized by heating to 1000°C[107,117]. Sol-gel glasses invariably crystallize as metastable hexacelsian unless positive steps are taken to

favour monoclinic celsian. Monoclinic celsian can be stabilized in the sol-gel glass-ceramic by the following methods.

2.13.2 Methods for Monoclinic Celsian

Seeding with Monoclinic Crystals

Monoclinic celsian can be formed by seeding glass frit with monoclinic crystals. By adding seed crystals to glass frit or to the gel prior to gelation and densification, monoclinic celsian is formed by epitaxial growth of seed crystals into the glass. Both celsian and rutile seed encouraged the growth of monoclinic celsian. For the sample containing 7.1 mol% of seeds heated to just below T_c (1075°C), monoclinic celsian arises just from the seed crystals eventhough some hexacelsian has already started to form at this temperature. After firing to just above T_c (1075°C), large amounts of both hexacelsian and monoclinic celsian are present. Longer heat treatments led to the gradual increase in the formation of monoclinic celsian suggesting that hexacelsian is transforming to monoclinic[107,111,112].

Doping with Li_2O

Monoclinic celsian can be obtained by doping gel glass with Li_2O. With increased Li_2O content the crystallization temperature of the <38μm diameter frit was reduced substantially and was only 876° C with 10 mol% Li_2O compared to 1055°C for undoped frit[112,113].

Prolonged Heat Treatment

Monoclinic celsian can be prepared by prolonged heat treatment of stoichiometric gel glass. Hexacelsian was the dominant phase crystallized from stoichiometric gel derived glass frit (<38 μm diameter) after heating above the peak temperature T_c, of crystallization exotherm and was still present after 1 to 20 hours at 1200°C. After long heat treatment it had completely converted to monoclinic celsian[118].
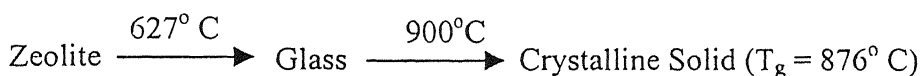
Cold Isostatic Pressing

Monoclinic celsian can be prepared by cold isostatically pressing glass powder followed by heat treatment. Little monoclinic celsian was detected in the samples pressed at 738 MPa and it was after 1 hour at 1200°C[117,119].

2.13.3 Methods for obtaining both Celsians

By Ion Exchange of Zeolites

Zeolites are hydrated aluminosilicates having the general formula $M_{2/n}^{n+}.Al_2O_3.xSiO_2.yH_2O$, where M is a cation, n and x are usually >2 and y varies from 0 to 10. Zeolite precursors were ion exchanged to replace the M cations with barium and subsequently heat treated to get the ceramic. For barium exchanged zeolites the transformation were identified as

$$\text{Zeolite} \xrightarrow{627^\circ\text{C}} \text{Glass} \xrightarrow{900^\circ\text{C}} \text{Crystalline Solid } (T_g = 876^\circ\text{C})$$

The crystalline solid that formed was either monoclinic or hexacelsian depending on the presence of minerlizers or seeds. Synthetic sodium zeolite 13X ($Na_{86}Al_{86}Si_{106}O_{384}.H_2O$) was used. The process was done in two steps where Na^+ ions were exchanged with ammonium ions and later were exchanged for Ba^{2+} ions. The ion exchange procedure consisted of suspending the zeolite powder in an aqueous solution of 10% weight ammonium nitrate, heating and continuously stirring at 90°C. The suspension was filtered and dried in an oven and the procedure was repeated to ensure a more complete exchange of ammonium ions for the Na^+ ions. The next step in the ion exchange process involved suspension of ammonium exchanged powders in an aqueous solution of 10% weight barium nitrate. Two barium exchanges were conducted by heating the suspension to 90°C, filtering and drying the powder. Sample obtained is referred to as Ba-X powder. The pellets were made out of this powder and were heated at various temperatures between 800°C and 1600°C where they were held for 4 hours. Heat treatment resulted in the formation of hexacelsian in the range 1000-1100°C. Extended high temperature heat treatment (>20 hour at 1550°C) were required to form monoclinic polymorph. The monoclinic phase of celsian was successfully crystallized from zeolite precursors by using combination of lithium and monoclinic seed particle additions to the same samples. Heat treatments of the resulting powder between 1100 and 1200°C for 6 hours resulted in complete transformation to monoclinic celsian[119,120].

Electrofusion Method

Pure barium carbonate and kaolin were used as the main raw materials. With the addition of some plastic clay they were mixed and kneaded into briquettes and precalcined at about 800°C. 150 kg of raw materials was charged into the electric arc furnace. As centre of charge around the electrodes melted, crystalline lumps of the synthesized fields amounting

to 60 kg each time were obtained. The remainder was unmolted and acted as a self refractory wall. The crystalline mass was separated and Laue X-ray photograph showed that this synthetic crystal belongs to hexagonal system crystallographically[105].

Hydrothermal Synthesis

The reagents used were barium hydroxide octahydrate, aluminium hydroxide gel and syston 2X, a stable sol of silica (30% by weight) in water. The aqueous gels were prepared by mixing together barium hydroxide and aluminium hydroxide gel with a little water and a mortar. The silica sol was then added from a graduated pipette and mixed. The resultant suspension was transferred to a stoppered conical flask with the remainder of the water and stirred for about an hour. 7 ml (about 0.5g dry weight) of oxides were measured into each autoclave[121]. The products obtained are of the composition $BaO.Al_2O_3.nSiO_2$ ($1<n<9$). For various values of n the temperature was varied between $110^\circ C$ and $450^\circ C$ and the duration of the experiment ranged from few hours to several weeks. Higher the value of n and lower the temperature, the longer is the time required for crystallization. The species produced in major and reproducible yield were celsian, hexagonal $BaAl_2Si_2O_8$, harmotome, and two unidentified zeolites[122].

Solid State Method

A melt of $BaAl_2Si_2O_8$ stoichiometric composition was prepared by melting morgan sand (SiO_2= 99.7%), aluminium oxide (Al_2O_3 = 99.7%) and $BaCO_3$ reagent at $1800^\circ C$ for 4 hours in a 80% Pt 20% Rh crucible. The crucible was then rapidly transferred to $1400^\circ C$, kept overnight and then removed to room temperature. At $1400^\circ C$, hexacelsian crystallized at the centre and bottom of the crucible. The two polymorphs were separated by hand picking[114].

2.14 Composites of Celsian

Like most glass-ceramic materials, BAS exhibits relatively low mechanical properties which limit its use in many structural applications. Room temperature strength values of the order of <100 MPa and the fracture toughness values of the order of <2.0 $MPa.m^{1/2}$ are typical[123]. Methods being explored to improve the mechanical properties of BAS are currently based on conventional ceramic-matrix composite processing methods where the reinforcement phase is added as discrete particulates or continuous fibers. The reinforcement of celsian matrix with Nicalon fibers having a duplex BN/SiC coating results

in strong and tough composite. Apparent flexural strength of 850-960 MPa and young's modulus of 1.65 GPa[124] have been observed. Recent research has concentrated on developing an in situ reinforced barium aluminosilicate (IRBAS) composite that offers high strength and toughness, low cost and ease of manufacturing. In situ reinforced BAS is produced by combining BAS forming powders with Si_3N_4 powders which, when processed develop a composite structure comprised of a barium aluminosilicate silicate matrix reinforced in situ with rod like grains of Si_3N_4[125]. The resulting composite material exhibited excellent mechanical and thermal properties compared to unreinforced BAS and approached those of Si_3N_4 due to high level of reinforcement which could be achieved. Flexural strengths up to 565 MPa and fracture toughness up to 5.74 MPa.m$^{1/2}$ were typical. Thermal property measurement showed the material to exhibit low coefficient of thermal expansion (3.8×10^{-6}/°C) and high thermal conductivity (9.19 W/(cm.K)), which provide good thermal shock resistance. In situ reinforced BAS appears to be a promising candidate for future high-temperature engineering applications.

2.15 Potential Applications

Barium aluminosilicate (BAS) is attracting considerable interest for diverse applications such as structural components, electronic packaging and matrices for ceramic-matrix composites due to its refractoriness, thermal properties and electrical properties[125]. It has a high melting temperature (about 1760°C)[119], low thermal expansion coefficient of 2.29×10^{-6} / °C[123] up to 1000°C and excellent phase stability up to 1590°C. These properties make it attractive for use as matrix material in ceramic matrix composites for power and propulsion system. Further the dielectric constant of celsian is 6.55 at room temperature and may also be used as a dielectric ceramic or in high temperature electromagnetic windows (radomes). It is used as substrates for microelectronics. It is used commercially in electrical porcelines, thick film, dielectric glass ceramics, whiteware glaze pigments, low expansion refractory glass ceramics and as grain boundary phase in high alumina ceramics[106].

2.16 Objective of this Work

Stoichiometric silicon carbide fibers are desired for reinforcement of ceramic and metallic matrix composites, especially those intended for high temperature applications, because of the favourable thermomechanical properties of SiC. Small diameter fibers, which can be produced by a polymer precursor route, are desired to impart flexibility to this high modulus material to permit weaving, braiding and knitting for preparation of preforms. In a pioneering study, Yajima and coworkers have shown that polycarbosilane (PCS) upon crosslinking can be converted into β-SiC by a two step heat treatment. The tedious synthetic procedure in the preparation of PCS limits its potential as a ceramic precursor. To overcome this difficulty alternative polymers have been tried. Notable among these is polysilastyrene which can be used as a precursor after crosslinking with UV light. This method again involves two steps to synthesize SiC. So an alternative method is desirable for the preparation of polymer precursor. In this study an attempt is made to prepare crosslinked polymers using divinyl benzene as the chemical crosslinking agent.

As discussed in the literature survey four crystalline polymorphs of $BaAl_2Si_2O_8$ have been recognized. Celsian and paracelsian, both monoclinic are known as natural minerals. The other two phases are encountered only in synthetic products, which are generally referred as high and low temperature modifications of hexacelsian. Celsian with a melt temperature of 1760°C is very difficult to prepare by container melting method. Thus a low temperature sol-gel route is a better method to synthesize celsian. Heat treatment of $BaAl_2Si_2O_8$ gels invariably results in the crystallization of hexagonal phase rather than monoclinic phase. However, monoclinic celsian is a preferred polymorph because of its high thermal stability, low thermal expansion and oxidation resistance. In this study, an attempt has been made to stabilize monoclinic celsian using various chemical additives.

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Chapter 3
Experimental

3.1 Materials for SiC Preparation

Dimethyldichlorosilane (Aldrich, USA), Phenylmethylsilane and Divinyl benzene (Fluka Chemika, USA) and Oleic acid (S.D Fine Chemicals, India) were used as received. Toluene employed in this work was purified and dried by standard literature procedures[1] and Styrene used was also vacuum distilled by literature procedure[2].

3.2 Polymer Preparation

3.2.1 Preparation of Crosslinked Polysilastyrene

A 500 ml, 2 necked round bottom flask, oven dried and flushed with nitrogen, was fitted with a reflux condenser, a heating mantle and an inlet and outlet for flushing nitrogen. Toluene and sodium were added to the flask, along with one or two drops of oleic acid which aid in dispersing the sodium. The toluene was refluxed and magnetic stirrer was used to create sodium dispersion. The heating mantle was removed and the dispersion in toluene was allowed to cool to $70^{\circ}C$, where upon mixture of Me_2SiCl_2, $PhMeSiCl_2$ and divinyl benzene was added dropwise using a pressure equalizing funnel, quickly enough to maintain the temperature at gentle reflux. The solution turned from gray to blue. After the addition was complete, the heating mantle was replaced and the reflux was maintained for 7 hours. At the end period, the heat was taken away, the reaction was cooled down to room temperature and the mixture was quenched adding approximately 30ml of methanol dropwise. The precipitate formed was filtered and washed with water three times (3×30 ml) and was dried in vacuum (10^{-3} torr at room temperature). The details of the amounts of various monomers used for the synthesis of various polymers are given in Table 3.1.

3.2.2 Preparation of Crosslinked Poly(tetramethyl disilylene-co-styrene)

For the preparation of the above polymer the same procedure as in section 3.2.1 was used. The only difference was that to the finely divided molten sodium, a monomer mixture containing dimethyldichlorosilane, styrene and divinylbenzene were added using a pressure

containing dimethyldichlorosilane, styrene and divinylbenzene were added using a pressure equalizing funnel. The reaction mixture was allowed to reflux gently for 6 hours. The details of the amount of various monomers used for the synthesis of various polymers are given in Table 3.1.

3.2.3 Preparation of Crosslinked Poly(dimethyldichlorosilane)

For the preparation of this polymer also same synthesis procedure as in section 3.2.1 was used. Here a monomer mixture of dimethyldichlorosilane and divinyl benzene was added to the finely divided sodium and the reaction mixture was allowed to reflux for 7 hours. The amounts of monomer used for the synthesis of this polymer are given in Table 3.1.

Table 3.1 Different SiC Precursors Synthesized in this Study.

Polymer	Monomers (moles, grams)	Toluene (ml)	Sodium (moles, grams)	Polymer obtained (grams)
Polymer 1	Me_2SiCl_2 (0.04, 5.16) MePhSiCl$_2$ (0.04, 7.65) Divinyl benzene (0.002, 0.26)	50 ml	0.18, 4.23	3.4
Polymer 2	Me_2SiCl_2 (0.04, 5.16) MePhSiCl$_2$ (0.04, 7.65) Divinyl benzene (0.005, 0.67)	50 ml	0.18, 4.23	4.0
Polymer 3	Me_2SiCl_2 (0.04, 5.16) MePhSiCl$_2$ (0.04, 7.65) Divinyl benzene (0.011, 1.42)	50 ml	0.18, 4.23	4.5
Polymer 4	Me_2SiCl_2 (0.04, 5.16) MePhSiCl$_2$ (0.04, 7.65) Divinyl benzene (0.017, 2.26)	50 ml	0.18, 4.23	5.7
Polymer 5	Me_2SiCl_2 (0.04, 5.16) Styrene (0.02, 2.08) Divinyl benzene (0.010, 0.81)	40 ml	0.08, 1.84	3.5
Polymer 6	Me_2SiCl_2 (0.04, 5.16) Styrene (0.02, 2.08) Divinyl benzene (0.017, 1.28)	40 ml	0.08, 1.84	5.0
Polymer 7	Me_2SiCl_2 (0.06, 7.74) Divinyl benzene (0.010, 1.37)	50 ml	0.12, 2.76	4.5

3.3 Pyrolysis

The various organic crosslinked polymers (polymer 1–7) were obtained as white powders. These polymers were pyrolized in a vaccum furnace at $1500^{\circ}C$ for 8 hours. After the pyrolysis, the powder turned gray and it was found to be sintered during pyrolysis owing to its large surface area. The pyrolized powders were characterized using techniques like X-ray diffraction, Electron probe micro analysis, Raman spectroscopy and Scanning electron microscopy. The details of these techniques are given in later sections.

3.4 Stabilization of monoclinic celsian

Sol–gel method was used for the preparation of hexacelsian ($BaAl_2Si_2O_8$). By chemically preparing the powder via a sol–gel technique, it is possible to obtain powders of good quality at low twmperature. The chemically prepared powder or monoliths exhibit high reactivity, extreme purity and ultrahomogenity. Such powders are suitable for a number of applications where traditional ceramic precursors are not suitable[3].

3.4.1 Materials for Preparation of Celsian

Tetraethylorthosilicate, aluminium secondary butoxide, lithium isopropoxide (Fluka chemika, USA), barium acetate (Proanalysi, India), TiO_2 (Nanophase), $SrCO_3$ (Albert Victor, India), isopropanol and acetic acid (Nice laboratory chemicals, India) were used for the synthesis as received. Crude ethanol was distilled before using it by standard literature procedures[1].

3.4.2 Reaction Set Up

$BaAl_2Si_2O_8$ (hexacelsian) was prepared by the reaction between tetraethylorthosilicate (TEOS), aluminium–sec–butoxide and barium acetate. The reaction was carried out under constant stirring condition in a 500ml two necked flask fitted with a reflux condenser. Equalizer funnel was used for the dropwise addition of chemicals. Using sol–gel method both stochiometric and non–stoichiometric powders were prepared. Inorder to stabilize $BaAl_2Si_2O_8$ in monoclinic form, chemical additives were added during synthesis of the gel or during sintering. The different additives which were used to stabilize monoclinic celsian are TiO_2, Li_2O and SrO_2. In case of TiO_2 presynthesized nanocrystalline powder was used. $LiOC_3H_7$ was used as a source of Li_2O whereas SrO_2 was added in the form of carbonate.

49

3.5 Composites of Hexacelsian with ZrO_2

ZrO_2 occurs in several forms like monoclinic, tetragonal, cubic and liquid form. There are two reversible transformation in zirconia. They are

$$1170^{\circ}C$$
Monoclinic $\leftrightarrow$ Tetragonal

$$2370^{\circ}C$$
Tetragonal $\leftrightarrow$ Cubic

The transformation from tetragonal to cubic form is not of much technological importance. Tetragonal to monoclinic transformation is very effective in improving toughness of weak matrices and imparts transformation toughening. This transformation is a martensitic type of transformation. In addition to martensitic transformation other factors which contribute to overall toughness are ferroelastic domain switching, crack deflection and crack bridging[4]. ZrO_2 was added to celsian to improve the overall toughness of the composite.

3.6 Characterization Techniques

3.6.1 X–Ray Diffraction Analysis

X–ray diffraction pattern for the samples were recorded by X–ray Diffractometer (RICH SIEFERT ISO DEBYEFLEX 2002, GERMANY) using Cu – $K_{1\alpha}$ radiation (λ = 1.54056 A°). The diffraction patterns were recorded at a scanning speed of 3° min^{-1} at room temperature. Diffraction patterns obtained were matched with standard ASTM powder diffraction files. Diffraction patterns were used to determine the grain size using standard procedure[5].

3.6.2 Electron Probe Micro Analysis

Qualitative analysis was done using a JEOL SUPER PROBE JXA 8600MX, Electron probe micro analyser. Samples were coated with Au–15% Pd. This coating was given to prevent charging of the sample. The analysing crystal and the L value for each element analysed is given in Table 3.2.

Table 3.2 L Values for the Various Elements Analysed

Element	Crystal Name	Crystal Designation	L Value(nm)
Si	Thallium acid phthalate	TAP	77.46
C	Lead stearate	STE	124.66
Ba	Pentaerythritol	PET	88.91
Ba	Lithium fluoride	LIF	193.03
Al	Thallium acid phthalate	TAP	90.66
Zr	Pentaerythritol	PET	194.43

3.6.3 Raman Spectra

Raman spectrum was recorded using SPEX-1877E Triplemate Monochromator. 5W Ar^+ laser ($\lambda_e = 515$ nm) was used as an excitation source and charge coupled detector (CCD) was used as the detector.

3.6.4 Scanning Electron Microscope

Samples were observed under a JEOL JSM 840A Scanning Electron Microscope. Samples were given Au–15% Pd coating. The coating was given to prevent charging of the sample. SiC, celsian and composite samples were observed to identify the microstructure and particle size distribution.

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Results and Discussions

Section A – Development of Precursors for SiC fibers

4.1 Need for Alternate Precursor to SiC

Silicon Carbide (SiC) is a highly valued ceramic material due to its many desirable properties such as oxidation resistance, low thermal expansion and high chemical stability. An increasing amount of research has been directed towards the synthesis of SiC from pyrolysis of organosilicon precursors. The advantage of precursors is that they can be spun into fibers, or used to coat carbon fibers or other substrates. Other forms of utility include use in ceramic matrix composites as well as in the form of powders. Subsequent processing of the polymer yields the desired ceramic or a mixture of ceramic phases depending on the pyrolysis condition. These include nature of the pyrolysis gas, temperature etc[1]. The first reports concerning the use of polysilanes have come from the group of Yajima and his coworkers. They discovered that polysilane polymers could be utilized as precursors for β silicon carbide[2-4]. Their process for making β-SiC begins with permethylpolysilane, which was synthesized by the dechlorination of dimethyldichlorosilane using sodium (reaction 1).

Reaction 1:

$$(CH_3)_2SiCl_2 \xrightarrow{\text{Na}} [(CH_3)_2Si]_n + NaCl$$
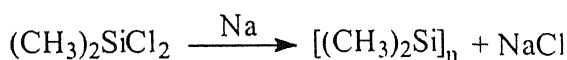
As noted earlier, this polymer is highly crystalline and insoluble in almost all the organic solvents and therefore cannot be processed readily[5]. However, it was found that when $(Me_2Si)_n$ is pyrolyzed above 400°C in an atmosphere of argon (reaction 2) a new soluble polymer was obtained.

Reaction 2:

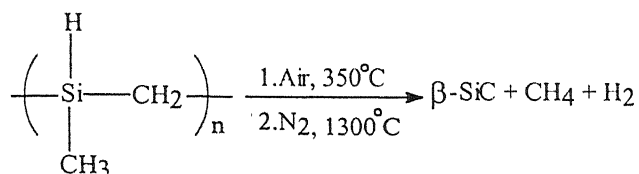$$[(CH_3)_2Si]_n \xrightarrow[\text{Ar}]{450\,^{\circ}C} \left(\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{Si}} - CH_2 \right)_n$$
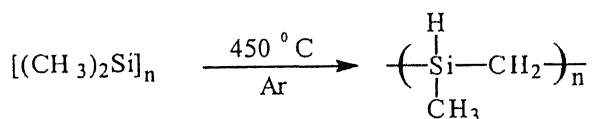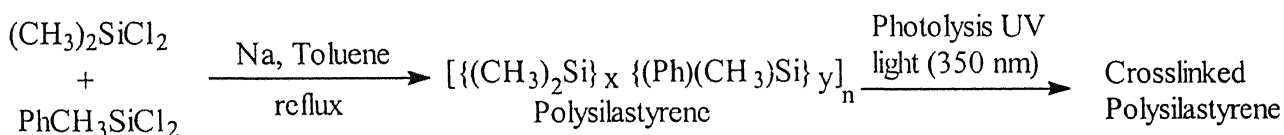
This polymer was named as polycarbosilane because of the alternating Si and C atoms in the backbone. It was noted that pyrolysis of $(Me_2Si)_n$ leads to a migratory nature of methylene unit to interrupt the polysilane chain, leaving behind a hydrogen on Si. These polycarbosilanes can

53

be crosslinked by surface oxidation in air and further pyrolyzed at 1300°C for one hour in a nitrogen atmosphere to obtain β-SiC[6,7] (reaction 3).

Reaction 3:

$$\left(\begin{array}{c} H \\ | \\ -Si-CH_2- \\ | \\ CH_3 \end{array}\right)_n \xrightarrow[\text{2.N}_2, 1300°C]{\text{1.Air, 350°C}} \beta\text{-SiC} + CH_4 + H_2$$

Inspite of their many attractive features the technological potential of polysilanes as ceramic precursors is however limited by the troublesome pyrolytic conversion to polycarbosilanes and fractionation. The latter is necessary to separate the higher molecular weight polycarbosilane from the oligomeric forms. It is not possible to use permethylpolysilane itself as a polymer precursor to ceramic as it is a highly crystalline white, incoherent powder, which decomposes before melting. An additional problem in the use of polycarbosilane lies in the fact that crosslinking of polycarbosilane involves exposure to air which introduces Si–O–Si linkages. The oxygen is retained in the ceramics processed from this source and it reduces the thermal stability of SiC. These drawbacks led to the search for an alternate precursor for SiC. Of the many alternate precursors studied mention must be made of polysilastyrene formed by the co-condensation of dimethyldichlorosilane and phenylmethylsilane. This polymer was crosslinked by UV radiation and then converted into silicon carbide.

$$\begin{array}{c} (CH_3)_2SiCl_2 \\ + \\ PhCH_3SiCl_2 \end{array} \xrightarrow[\text{reflux}]{\text{Na, Toluene}} \underset{\text{Polysilastyrene}}{[\{(CH_3)_2Si\}_x \{(Ph)(CH_3)Si\}_y]_n} \xrightarrow[\text{light (350 nm)}]{\text{Photolysis UV}} \begin{array}{c} \text{Crosslinked} \\ \text{Polysilastyrene} \end{array}$$

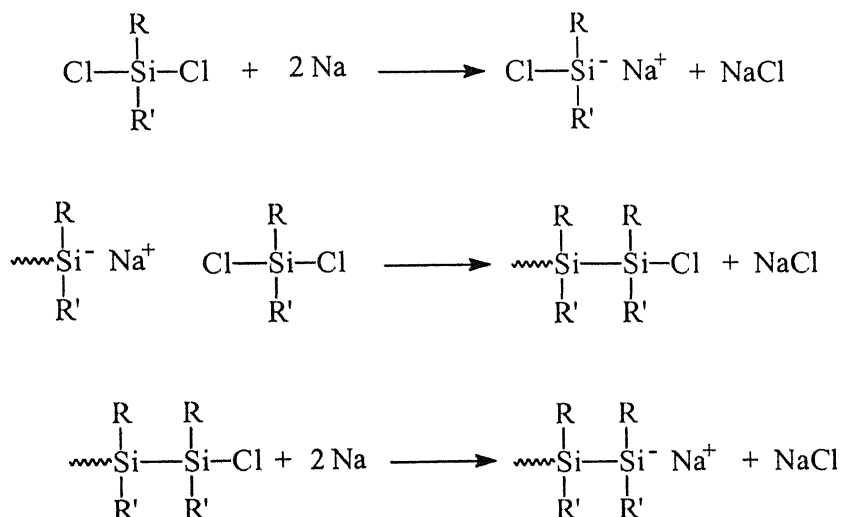When the crosslinked polysilastyrene is heated to higher temperature it results in the formation of β-SiC[7].

As can be seen from the above discussion the use of polysilastyrene reduces one step in the synthesis of β-SiC[8]. It would be however more desirable to obtain the polymer precursor of β-SiC in a single step. Towards this end we have pursued a synthetic strategy of utilizing a chemical crosslinking agent viz., divinyl benzene. Results obtained are presented below.

4.2 Synthesis of Crosslinked Polysilanes

We have synthesized three types of crosslinked polymer (1) Phenylmethyldichlorosilane (PhMeSiCl$_2$) and dimethyldichlorosilane (Me$_2$SiCl$_2$) were copolymerized together in the presence of small amounts of divinyl benzene by dechlorination reaction involving sodium. By this methodology we obtained the crosslinked polymers in the form of white powders. (2) Dimethyldichlorosilane, styrene and divinylbenzene were copolymerized to obtain crosslinked poly(tetramethyldisilylene–co–styrene). (3) We have also explored the possibility of using only dimethyldichlorosilane as the silane monomer and have successfully obtained crosslinked polymer incorporating divinyl benzene as the crosslinking agent. This last method is particularly important in view of the known intractability of (Me$_2$Si)$_n$. The synthetic strategy for obtaining the polymers and their yields are shown in the experimental section (Table 3.1). All the polymers are white powders. The nature of polymers i.e. their insolubility in the organic solvents suggest that these are extensively crosslinked. Furthermore, pyrolysis of these polymers leads to β-SiC, confirming that the polymer contains the silicon atoms in the backbone. The mechanism of polymerization is believed to occur as follows. This mechanism is based on the one proposed by West and coworkers[9].

4.3 Mechanism of Polymer Formation

The various mechanistic steps involved in the formation of polysilane polymers are given below.

$$
\text{Cl}-\underset{\underset{\text{R'}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}-\text{Cl} \ + \ 2\,\text{Na} \ \longrightarrow \ \text{Cl}-\underset{\underset{\text{R'}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}^-}}\ \text{Na}^+ \ + \ \text{NaCl}
$$

$$
\text{ww}\underset{\underset{\text{R'}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}^-}}\ \text{Na}^+ \quad \text{Cl}-\underset{\underset{\text{R'}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}-\text{Cl} \ \longrightarrow \ \text{ww}\underset{\underset{\text{R'}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}-\underset{\underset{\text{R'}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}-\text{Cl} \ + \ \text{NaCl}
$$

$$
\text{ww}\underset{\underset{\text{R'}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}-\underset{\underset{\text{R'}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}-\text{Cl} \ + \ 2\,\text{Na} \ \longrightarrow \ \text{ww}\underset{\underset{\text{R'}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}-\underset{\underset{\text{R'}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}^-}}\ \text{Na}^+ \ + \ \text{NaCl}
$$

In this mechanism, the initiation step (Step 1), thought to be very slow, is the reaction of $RR'SiCl_2$ with sodium to produce the ion pair $RR'SiCl^-$, Na^+. The propagation step (Step 2) which is fast but nevertheless, rate determining, is the reaction of anion-terminated chains with dichlorosilane to add one silicon unit and produce a chlorine ended chain. The latter is thought to be reduced rapidly to anionic form by reaction with sodium. The polysilane chains will alternately be terminated with silyl anions or Si – Cl. This mechanism can be elaborated as shown below:
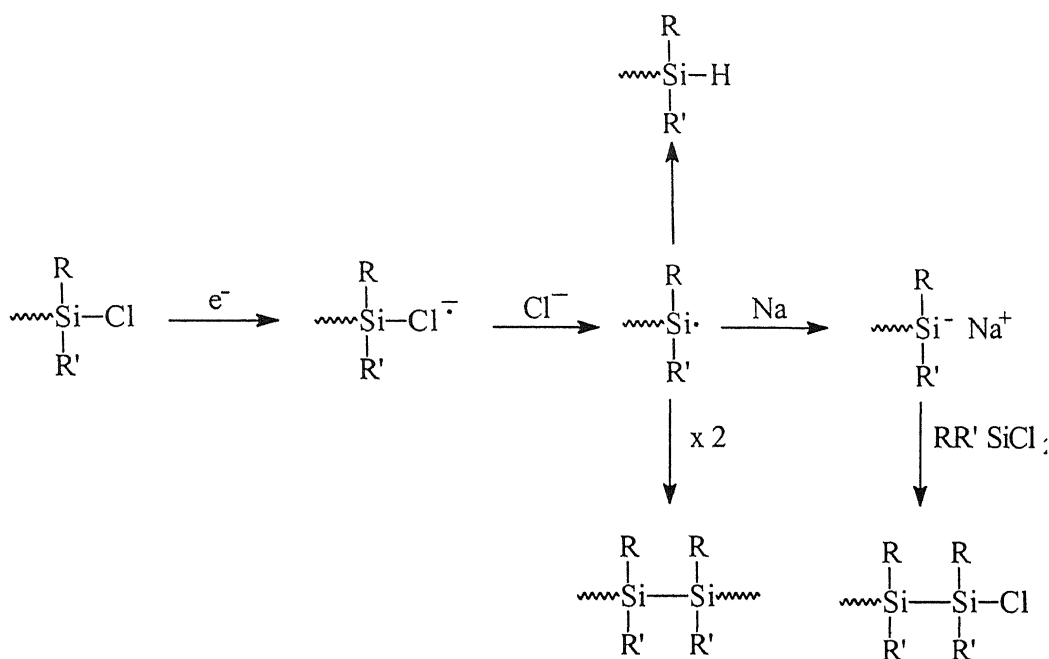
The reaction of chlorosilanes with sodium proceeds by an initial single electron transfer to form an anion radical, which loses a chloride ion rapidly to form a silyl radical. The latter may be reduced in another electron transfer step to give a silyl anion, which may either be bound to the sodium surface or be present in solution as an ion pair. The anion could then react with an Si–Cl bond which is the major reaction leading to chain extension. However, the silyl radical might be directly involved in chain extension by combination with another radical, or would add to a carbon-carbon double bond, or accept a hydrogen atom from the solvent to give an Si–H terminated chain.

Based on the above mechanism, we propose a similar mechanism in the present system keeping in mind the following differences:

1) It has been shown by Ramarao and coworkers[10] that in the copolymerization of Me_2SiCl_2 and styrene a disilyl species is mainly responsible for the polymer propagation.

2) It is also known that silyl radicals are more reactive than the styryl radical.

3) It is to be noted that divinyl benzene can be polymerized at two ends and hence crosslinking can be effective. The following mechanism illustrates the formation of the disilyl radical unit, which is responsible for propagation of the chain.

Silyl radical anion   Silyl radical

Dihalogenated species containing Si-Si bond   Disilyl radical anion   Disilyl radical

Based on the above mechanism the proposed structures for the polymers prepared in this study are given by Schemes 1, 2, 3.
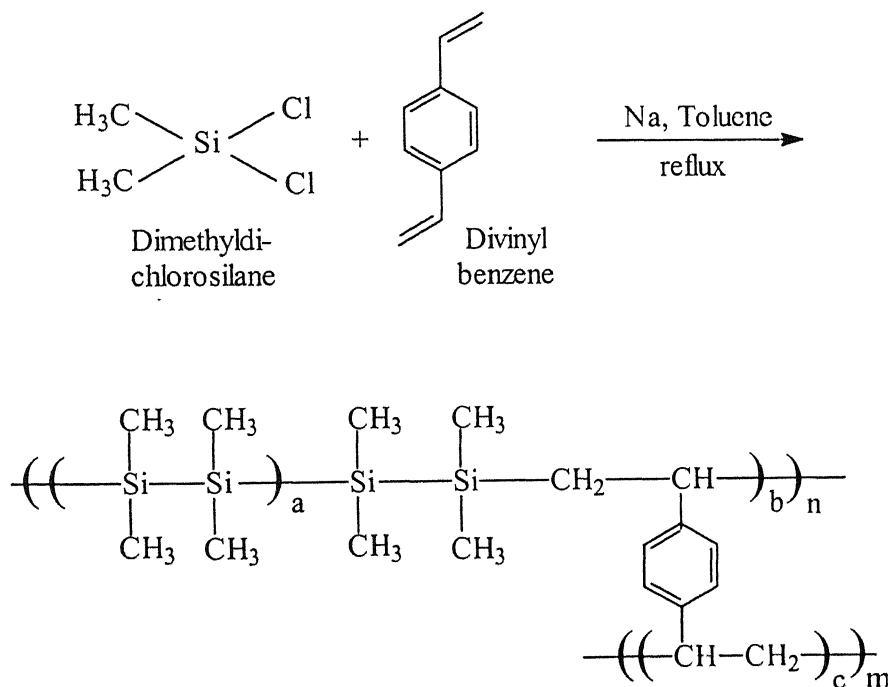
Scheme 1 Polymerization of Phenylmethylsilane and Dimethylsilane in the presence of Divinylbenzene.
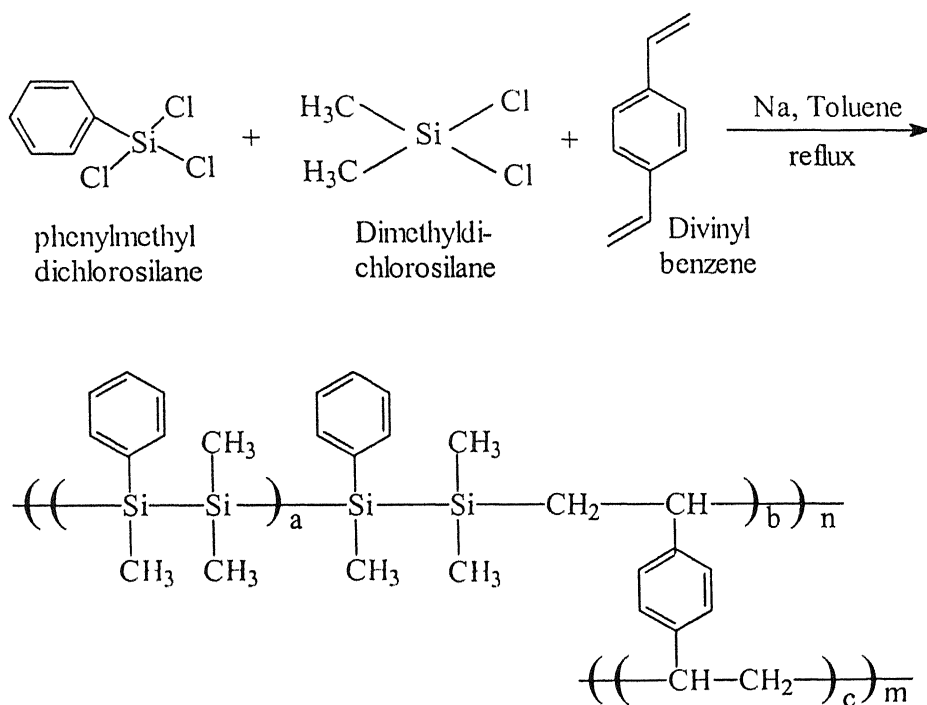
Scheme 2 Polymerization of Styrene and Dimethyldichlorosilane in the presence of divinyl benzene.
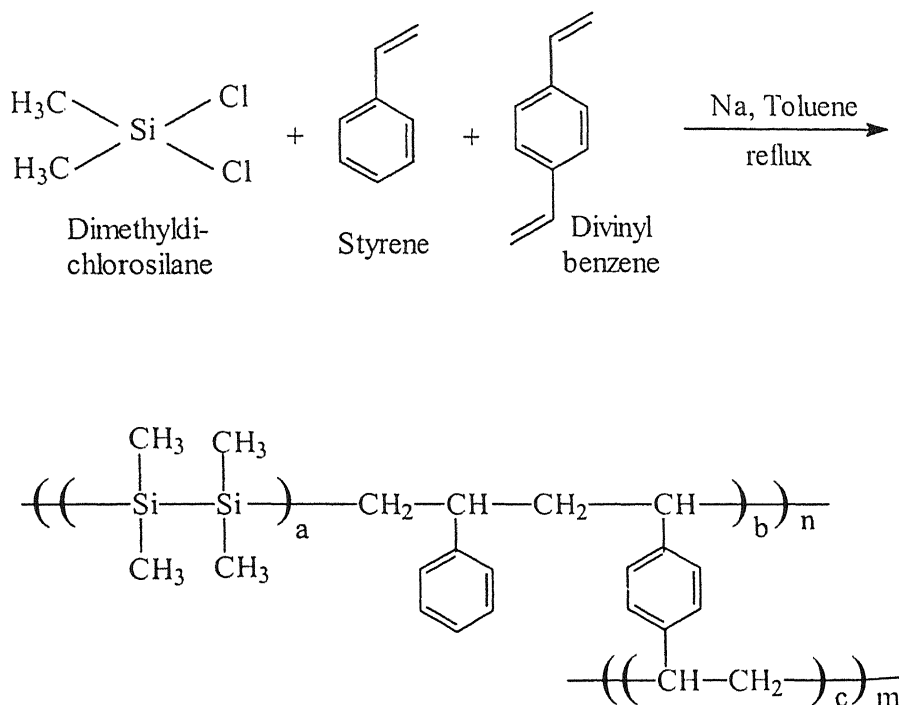
Scheme 3 Polymerization of Dimethyldichlorosilane in the presence of Divinylbenzene.

4.4   Conversion of Crosslinked Polymer Precursors to β-SiC

All the crosslinked polymers were heated at $1500^\circ C$ for 8 hours to convert the polymer into a ceramic. It was found that polysilastyrene crosslinked with 2% divinyl benzene got melted and could not be pyrolyzed into a ceramic. All the polymers which were crosslinked using 5% or more of divinyl benzene could be successfully pyrolyzed into a ceramic.

4.5   Characterization of the Pyrolyzed Powders

4.5.1 X–Ray Diffraction Analysis

X-ray diffraction analysis of all the pyrolyzed sample showed three distinct peaks at 35.7°, 60.2° and 71.6° which correspond to the (hkl) planes (111), (220) and (311) respectively of β-SiC thus confirming its formation from the crosslinked polymers. The X-ray diffractograms of β-SiC obtained from various polymer precursors are shown in Figs 4.1 – 4.3.

The grain size was roughly estimated from Bragg–peak broadening of (111) peak according to the formula

$$L = 0.9 \, \lambda \, / \, \beta \, Cos\theta$$

Where

> L = Average crystalline diameter.
> λ = Wavelength of X-rays.
> β = Half width of the X-ray peak.
> θ = Bragg angle of X-ray peak.

Line widths were corrected for instrument broadening with silicon standards according to the standard procedure[11]. Table 4.1 shows the grain size obtained from each of the crosslinked polymer
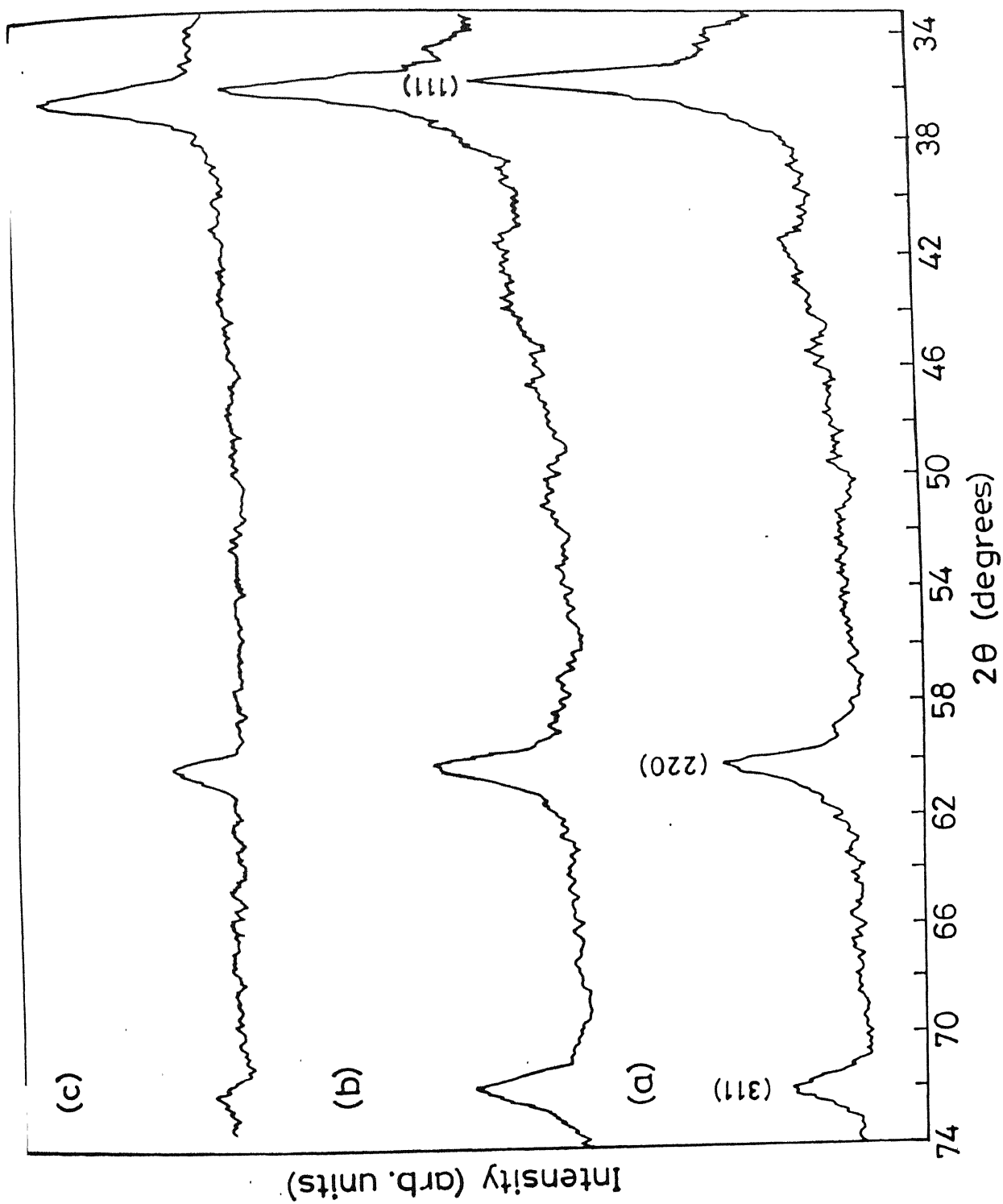
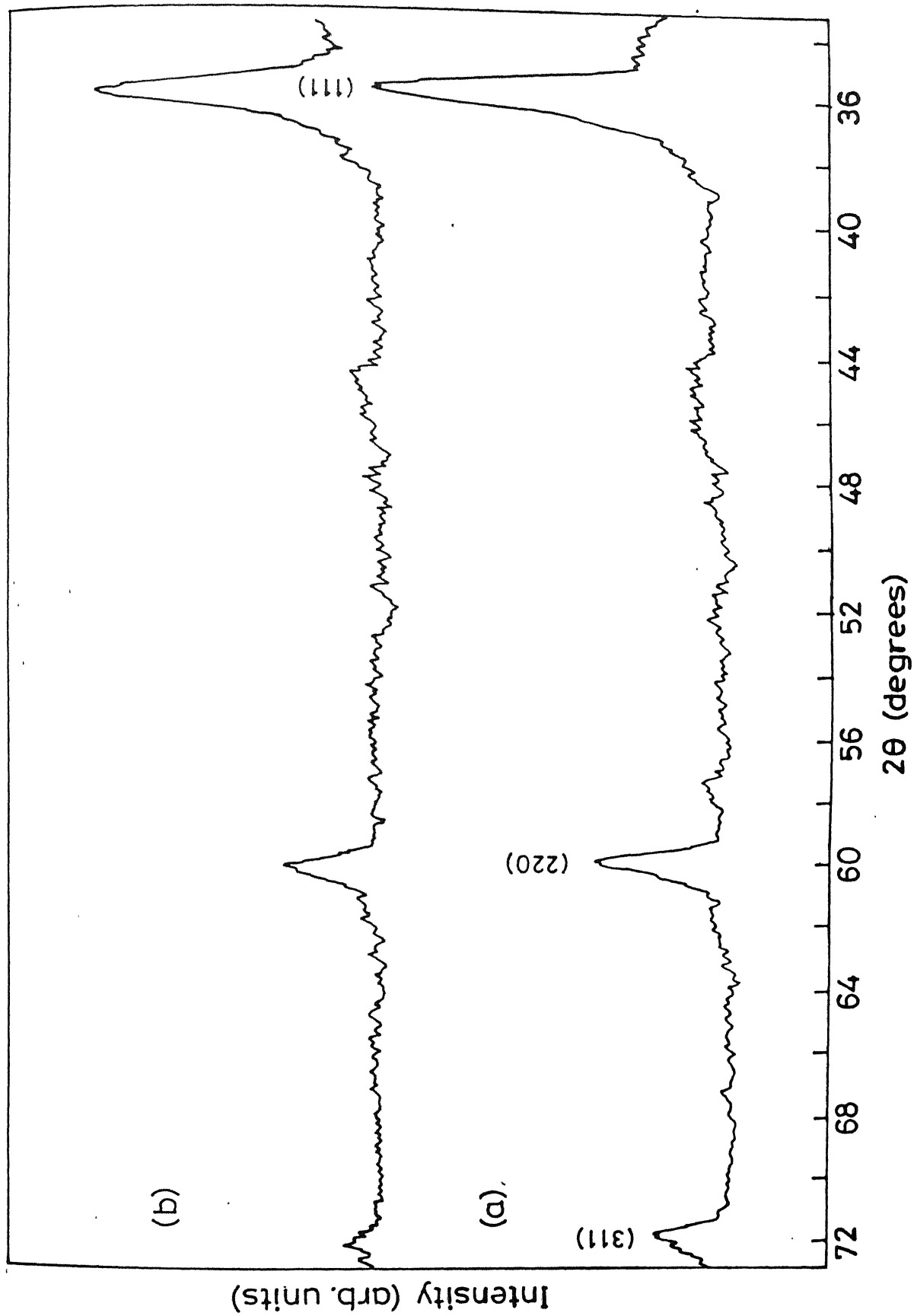Fig 4.1: X-Ray Diffraction Pattern of β-SiC from (a) Polymer 2 (b) Polymer 3 (c) Polymer 4

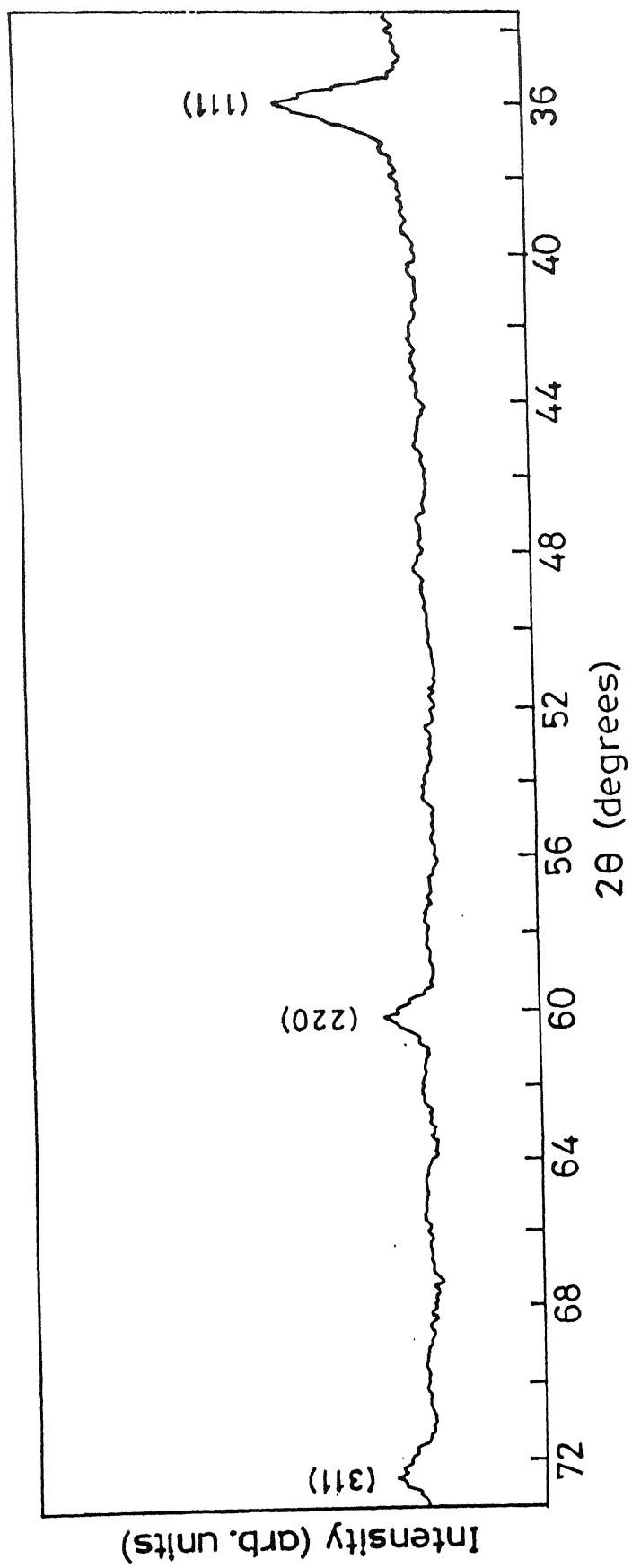Fig 4.2: X-Ray Diffraction Pattern of β-SiC from (a) Polymer 5 (b) Polymer 6

Fig 4.3: X-Ray Diffraction Pattern of β-SiC from Polymer 7

Table 4.1 Grain size of β-SiC obtained from Various Crosslinked Polymers after pyrolysis

β-SiC obtained from Polymer( )	Grain Size (nm)
Polymer 1	12.77
Polymer 2	8.72
Polymer 3	12.89
Polymer 4	19.36
Polymer 5	10.71
Polymer 6	11.90

After sintering at 1500°C for 8 hours, the grain size varied between 8–20 nm. This nanocrystalline SiC has important applications because of the significant improvement in ceramic nanocomposite mechanical properties compared with micrometer-sized particles prepared by Acheson process or by chemical vapour deposition.

4.5.2 Electron Probe Micro Analysis

EPMA analysis was done to further confirm the formation of SiC in pyrolyzed material. EPMA spectra of β-SiC obtained from the polymers show characteristic peak at 124.66, showing the presence of C and a peak at 77.46, showing the presence of Si. Figs 4.4, 4.5 (a&b) show the EPMA analysis spectrum of β-SiC obtained from polymer precursors.

4.5.3 Raman Spectroscopy

The Raman spectra of β-SiC samples are shown in Fig 4.6 (a&b). Absorption bands around 790 and 970 cm^{-1} which are characteristic of β-SiC are clearly seen.

4.5.4 Scanning Electron Microscopy

SEM micrograph of β-SiC in the secondary mode show that the pyrolyzed sample is sintered when it is heated at 1500°C for 8 hours. SEM micrographs of β-SiC obtained from the crosslinked polymers are shown in Figs 4.7 (a-d). The fine grains of β-SiC have sintered to

form three dimensional network. The residual porosity in between these networks is also visible in the micrographs.

4. 5. 5 Discussion

We have reported a simple strategy to prepare crosslinked polysilanes in a one pot synthesis. As already seen, our methodology relied on the use of divinyl benzene as a comonomer in small percentages along with diorganosilanes in the presence of sodium. Divinyl benzene was found to act as an effective crosslinking agent as it had two functional groups which can involve in polymerization process. The reaction of Me_2SiCl_2 and divinylbenzene in the presence of molten sodium in boiling toluene proceeded smoothly to afford a crosslinked polymer. This reaction also proceeded in the presence of a second monomer such as phenylmethyldichlorosilane or even styrene. The structure of these polymers, proposed by keeping in mind the mechanism of RamaRao. et. al. shows that they comprise of long polysilane chains containing Si – Si bonds interrupted by –CH(R) – CH$_2$ – linkages. All these crosslinked polymers have been found to afford β-SiC when heated in vacuum at 1500°C for 8 hours. X-ray diffraction analysis, Electron micro probe analysis and Raman spectra clearly shows that the ceramic obtained corresponds to β-SiC. Eventhough 2% divinl benzene crosslinked polymer was insoluble in common solvents it could not yield β-SiC. This is because of insufficient crosslinking and bonds break when heated to 1500°C. SEM micrographs clearly show that β-SiC is an aggregate of ultrafine particles and the grain size of β-SiC is in the nanometer range making it suitable for applications in the composite technology. The nanocrystalline morphology of the grains should improve the mechanical properties of SiC reinforced composites.
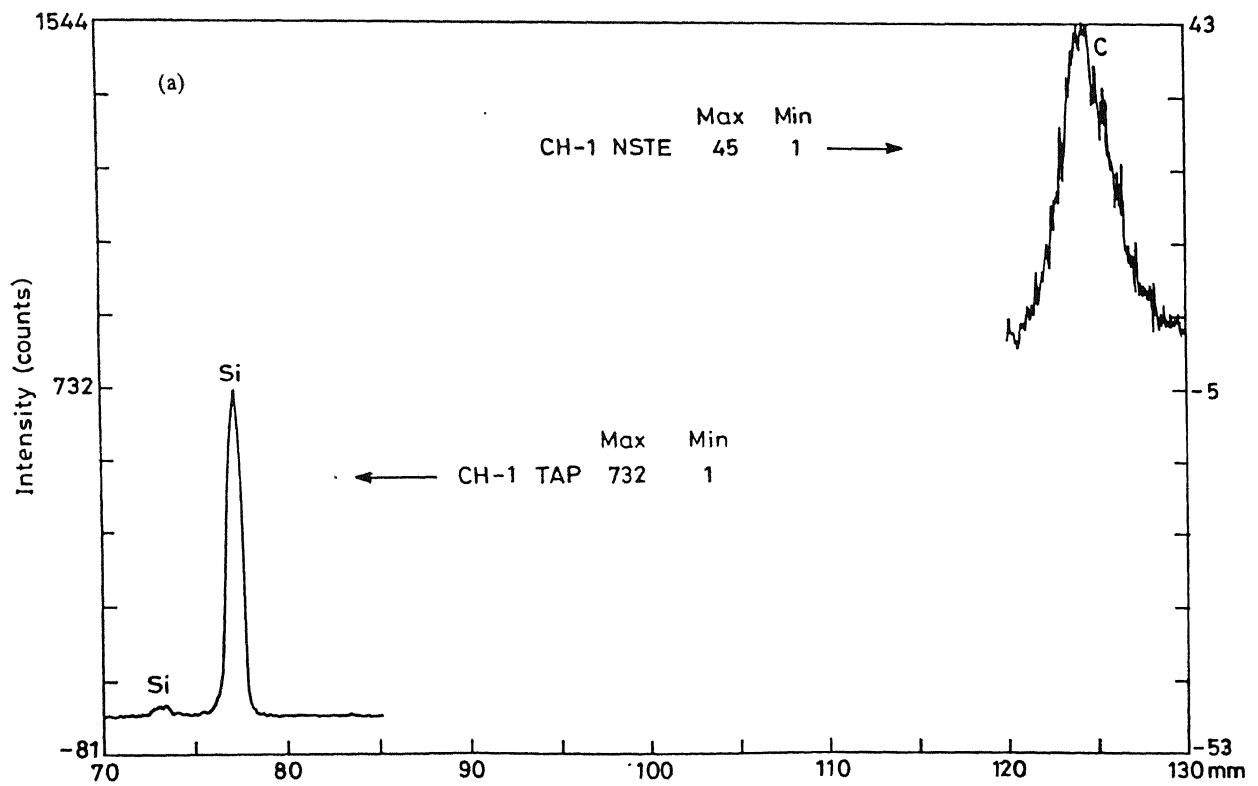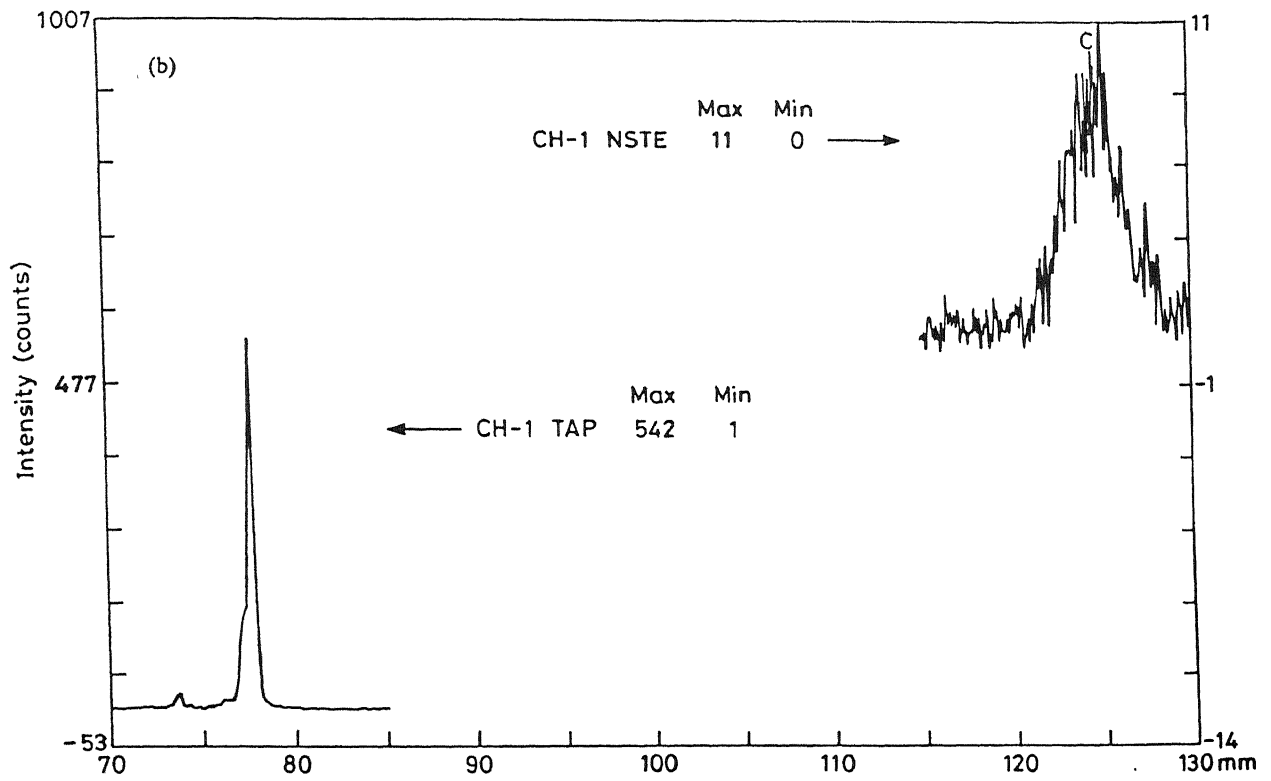
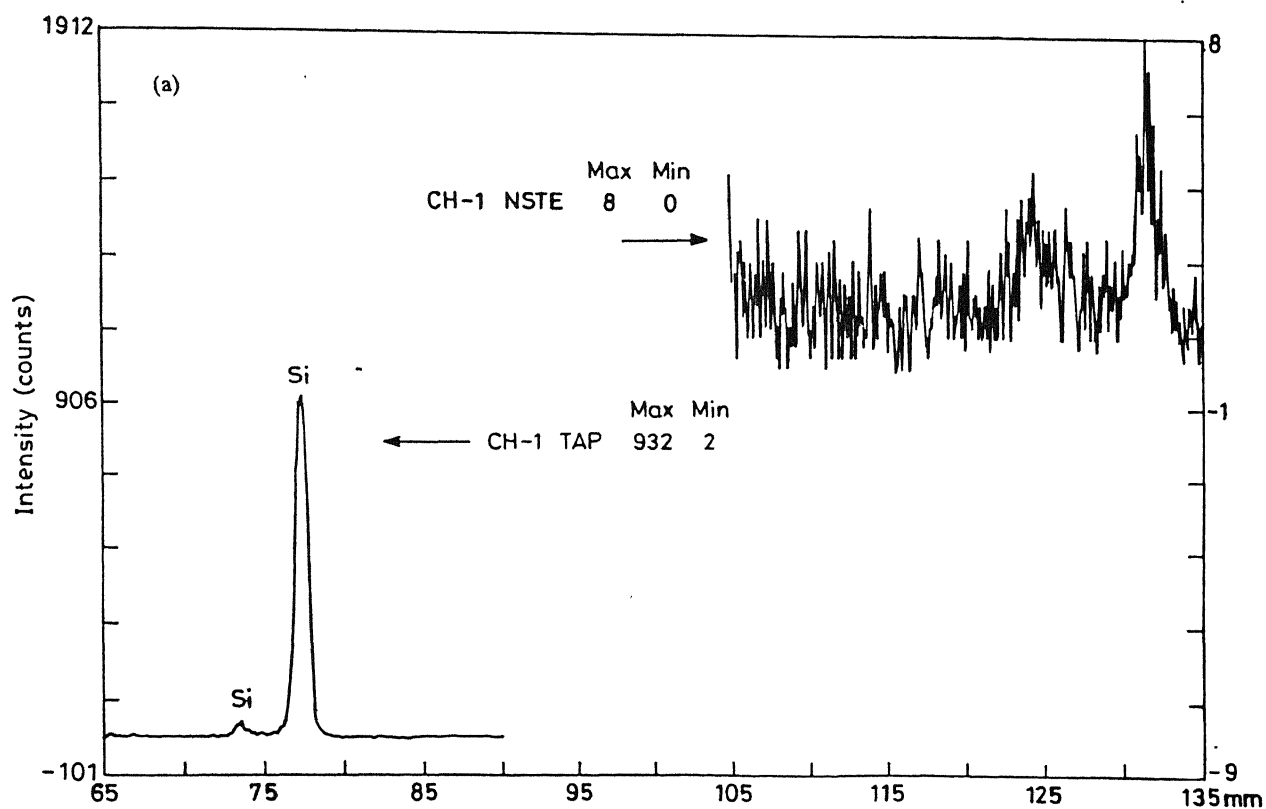Fig 4.4: EPMA Analysis Spectrum of β-SiC from (a) Polymer 2 (b) Polymer 3
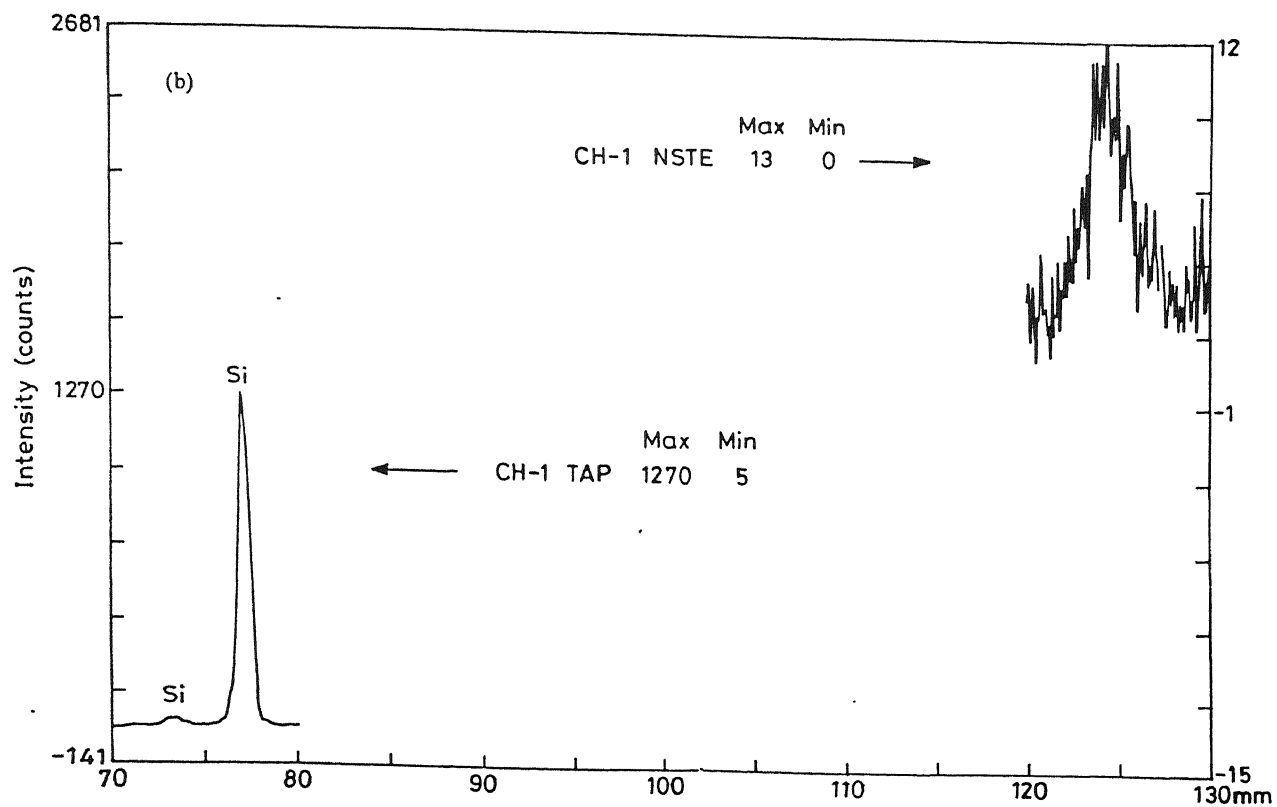
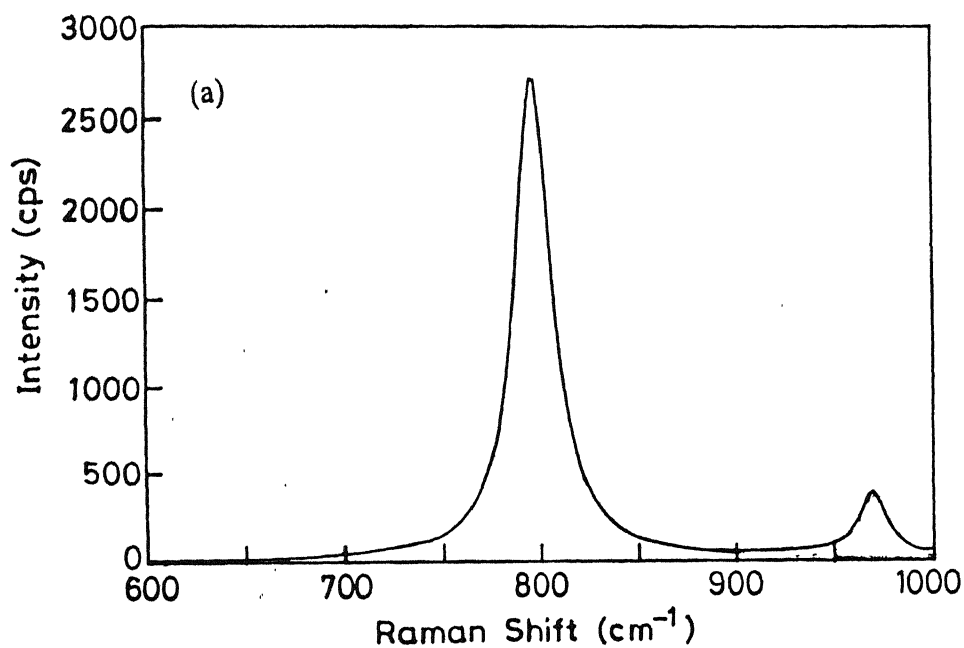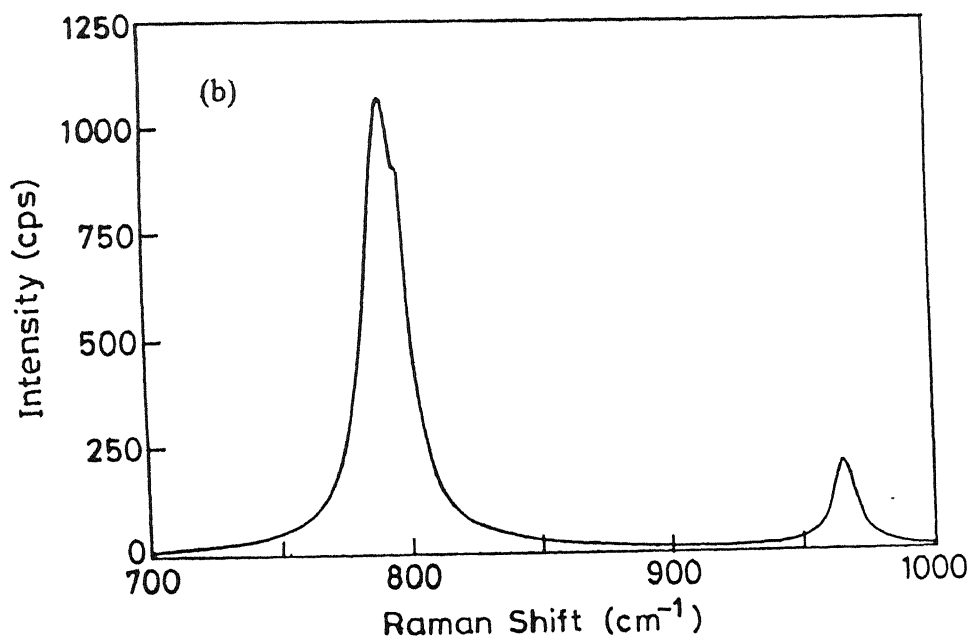Fig 4.5: EPMA Analysis Spectrum of β-SiC from (a) Polymer 5 (b) Polymer 7

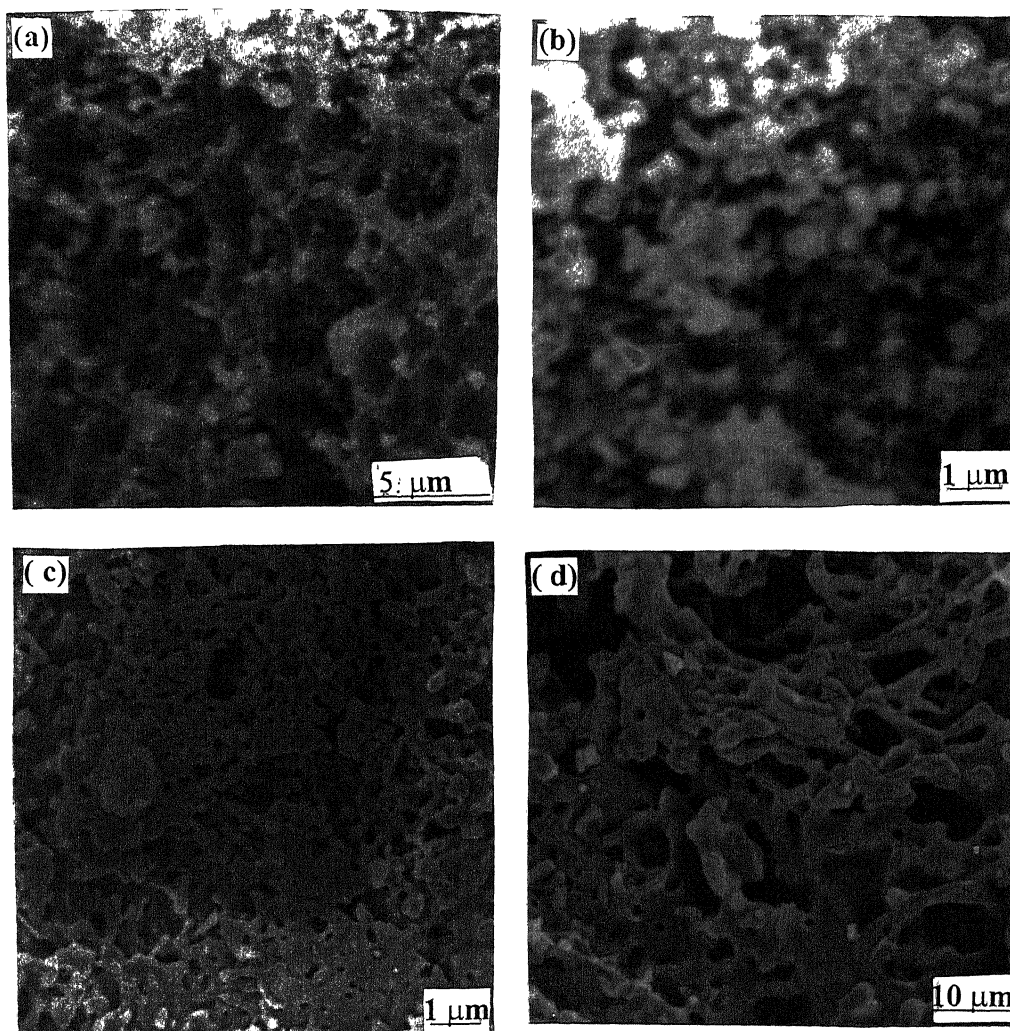Fig 4.6: Raman Spectrum of β-SiC obtained from (a) Polymer 3 (b) Polymer5

Fig 4.7 SEM Micrographs of β-SiC after Pyrolysis at 1500°C for 8 hours from (a) Polymer 2
(b) Polymer 3 (c) Polymer 5 (d) Polymer 7.

Section B Stabilization of Monoclinic Celsian.

Low cost ceramic composite materials that exhibit high strength and toughness, high thermal shock resistance and good oxidation resistance are attracting considerable interest for emerging high-temperature advanced engineering applications. Glass-ceramics are of particular interest because of their high melting temperature, low thermal expansion, oxidation resistance and low dielectric constant. These materials are also characterized by low raw material and processing costs, the latter a result of the ability to achieve high density without the use of expensive hot pressing or hot isostatic pressing commonly used to fabricate other structural materials[12]. Of the glass-ceramic being considered for high temperature applications, barium aluminium silicate ($BaO.Al_2O_3.SiO_2$) is one of the most promising because of the special properties it exhibits, which was described earlier in Chapter 2. The results of the sol-gel method used for the synthesis of hexacelsian and monoclinic celsian are presented below:

4.6   Synthesis of Barium Aluminium Silicate Gel

$BaAl_2Si_2O_8$ gel was prepared by the reaction between tetraethylorthosilicate, aluminium secondary butoxide and barium acetate. Synthesis of this gel involved three steps. For the synthesis of 15g scale of this gel, the first step involved preparation of dilute solution of TEOS and ethanol (17.48 ml of TEOS in 41 ml of ethanol). Partial hydrolysis was initiated by adding 1.41 ml of water (1/4 theoritical) to this solution. A few drops of 1N HCl was added to catalyze the hydrolysis. The solution was refluxed at $60^{\circ}C$ for 3 hours and was allowed to cool to room temperature. Step 2 consisted of slowly adding a dilute solution of aluminium secondary butoxide in isopropanol (20.1 ml of $Al(OsecC_4H_9)_3$ in 60 ml of isopropanol). This solution was allowed to react for 12 hours to ensure complete reaction. In step 3, 10g of barium acetate was dissolved in 6.7ml of water. Acetic acid was added to the barium acetate/water solution until the pH was lowered to 3–4 , after which the barium acetate/water solution was slowly added to TEOS/Aluminium secondary butoxide mixture. Any resulting barium acetate precipitate was taken back into solution with the addition of more acetic acid. This was then stirred for 10–15 minutes or until the solution became slightly translucent, indicating the onset of gelation. At this point the solution was cast into petri dishes. The gels were allowed to dry for 14 days. The flowchart for the above synthesis is given in Fig 4.8. The dried gel was crushed with a mortar

and pestle to break up the larger pieces and to reduce the gel into a fine powder and this powder was calcined in air at 600°C for 12 hours. The powder was pelletized using a ½ inch die. Five pellets of the same size were made and they were heated at 800°C, 1000°C, 1200°C, 1400°C and 1500°C for 8 hours in a furnace and these pellets were then characterized as described in the following section.
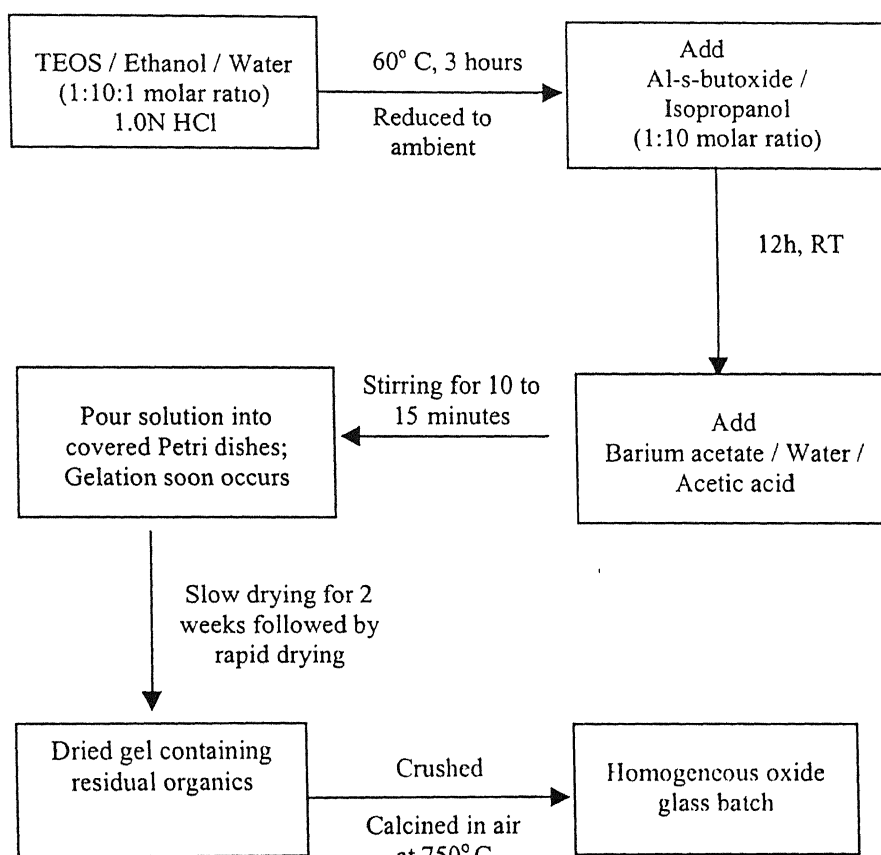
```
┌──────────────────────┐   60° C, 3 hours      ┌──────────────────────┐
│  TEOS / Ethanol /     │ ─────────────────▶   │        Add            │
│  Water                │                       │  Al-s-butoxide /      │
│  (1:10:1 molar ratio) │   Reduced to          │  Isopropanol          │
│  1.0N HCl             │   ambient             │  (1:10 molar ratio)   │
└──────────────────────┘                       └──────────────────────┘
                                                           │
                                                           │ 12h, RT
                                                           ▼
┌──────────────────────┐  Stirring for 10 to   ┌──────────────────────┐
│  Pour solution into   │  15 minutes           │        Add            │
│  covered Petri dishes;│ ◀─────────────────    │  Barium acetate /     │
│  Gelation soon occurs │                       │  Water / Acetic acid  │
└──────────────────────┘                       └──────────────────────┘
         │
         │ Slow drying for 2
         │ weeks followed by
         │ rapid drying
         ▼
┌──────────────────────┐   Crushed             ┌──────────────────────┐
│  Dried gel containing │ ─────────────────▶   │  Homogeneous oxide    │
│  residual organics    │                       │  glass batch          │
│                       │   Calcined in air     │                       │
│                       │   at 750° C           │                       │
└──────────────────────┘                       └──────────────────────┘
```

Fig 4.8: Flowchart for the Synthesis of Hexacelsian[12]

4.6   Characterization of Hexacelsian

4. 7. 1 X–Ray Diffraction Analysis

X–ray diffraction analysis showed that 800°C was not enough for the complete formation of hexacelsian $BaAl_2Si_2O_8$. At 1000°C, distinct hexacelsian peaks were observed , the intensity of which increased on heating to 1500°C. The X-ray diffraction patterns of the gel heated to various temperatures are shown in Fig. 4.9. Grain size was determined using the symmetrical (101) peak by the formula as in section 4.5.1. Grain size was found to be 59.4 nm for the pellet heated at 1500°C for 8 hours.

4.7.2 Electron Probe Micro Analysis

Qualitative analysis using EPMA showed peak at 88.91, confirming the presence of barium, peak at 90.66 confirmed the presence of aluminium, peak at 77.46 confirmed the presence of Si, further confirming the formation of barium aluminium silicate. Fig 4.10 shows the EPMA analysis pattern of barium aluminium silicate.

4.7.3 Scanning Electron Microscopy

Scanning electron micrograph of the sintered pellet at 1500°C for 8 hours is shown in Fig 4.11. It shows 10 μm hexagonal shaped plates of hexacelsian.

4.8   Composites of Hexacelsian

ZrO_2 is added to hexacelsian to increase the toughness of hexacelsian. The reason for the addition of ZrO_2 is explained in the experimental section. To 1g of the calcined gel we add 0.25g (20%) of ZrO_2. This was pelletized using a ½ inch die. Similarly, a pellet was made of 1g calcined gel by adding 0.67g (40%) of ZrO_2. Both these pellets were heated at 1500°C for 8 hours. The pellets were furnace cooled to 1000°C. At 1000°C the pellets were taken out and cooled to room temperature. This was done for the retention of tetragonal phase which was very important for improving the strength of hexacelsian. Both these pellets were analysed as described in Section 4.9.
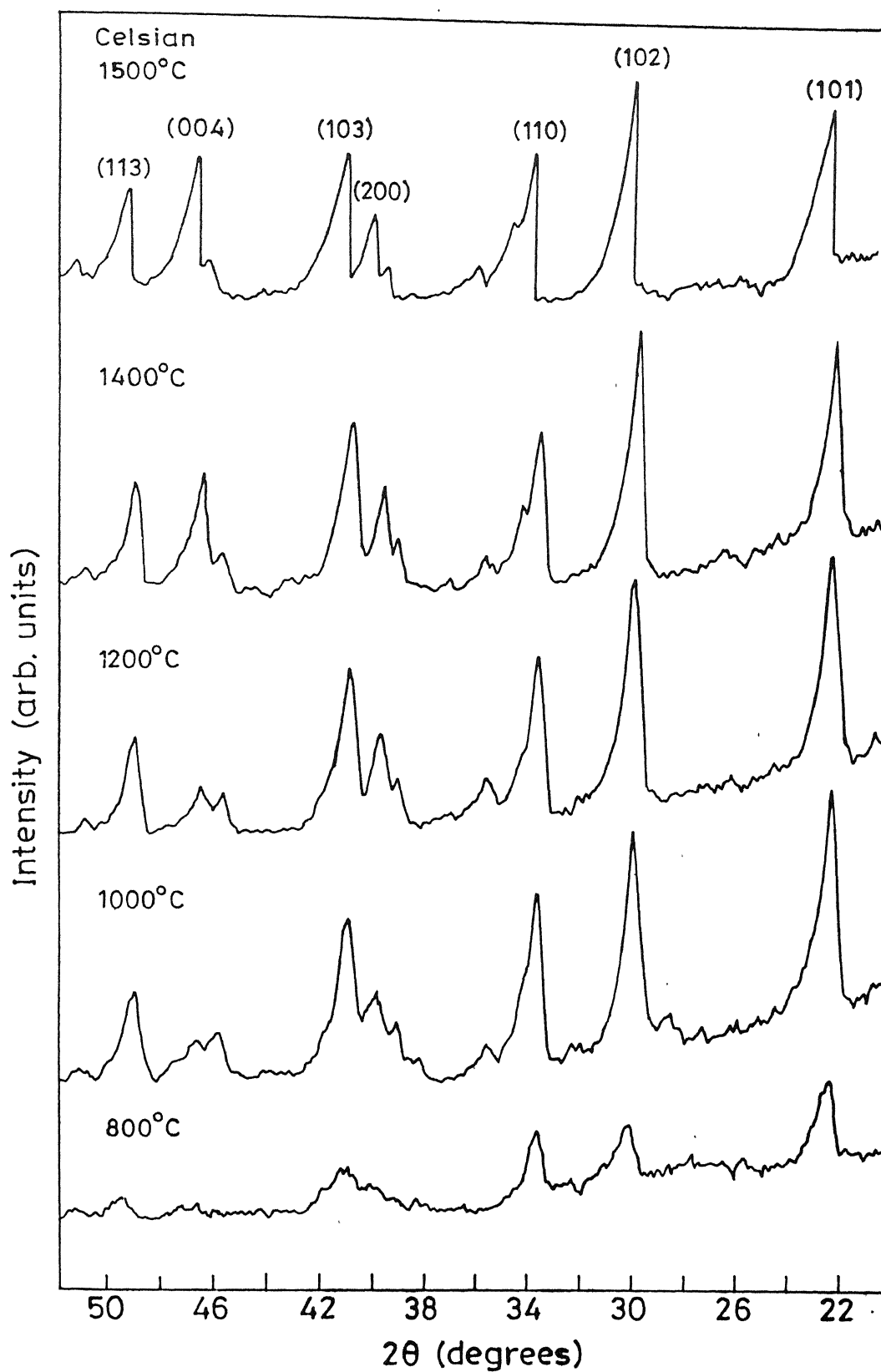
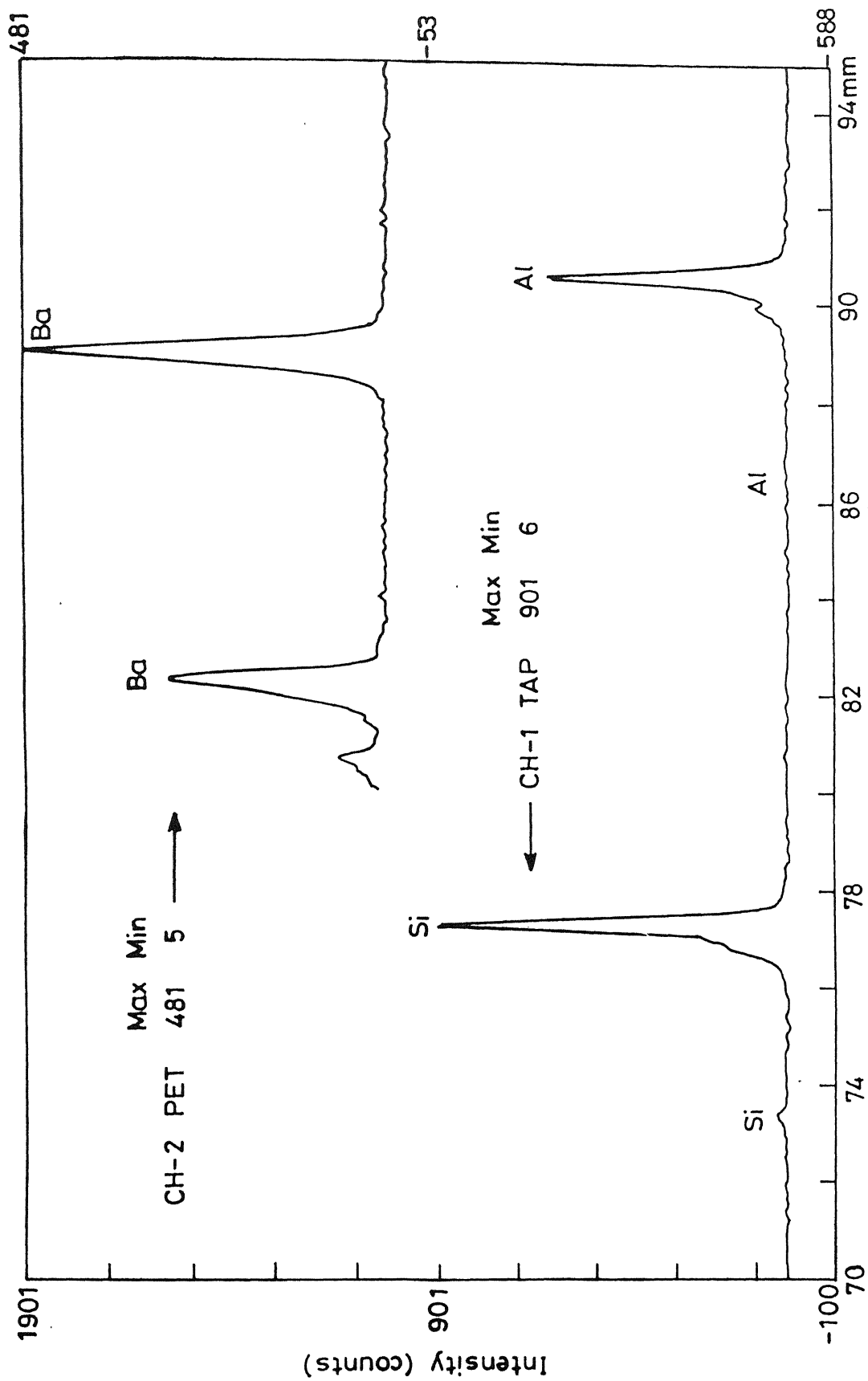Fig 4.9: X-Ray Diffraction Pattern of Hexacelsian Sintered at Various Temperature

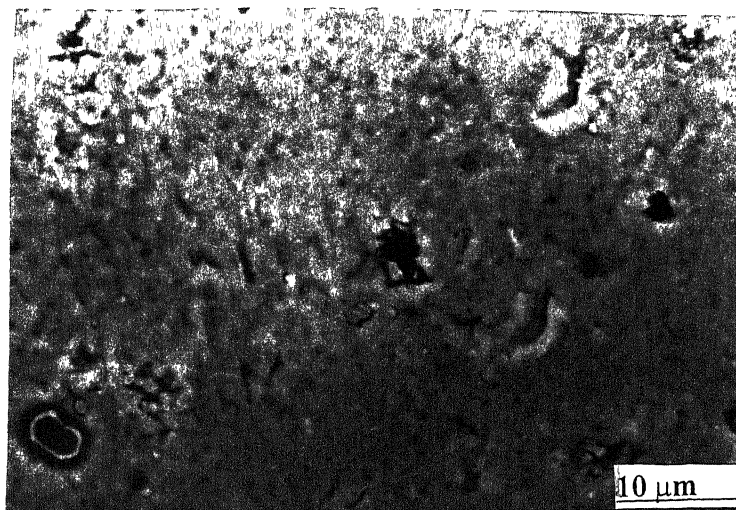Fig 4.10: EPMA Analysis Spectrum of Hexacelsian (BaAl$_2$Si$_2$O$_8$)

74

Fig 4.11 SEM Micrograph of Hexacelsian (Sintered at 1500°C for 8 Hours)

4.9 Characterization of Hexacelsian – ZrO$_2$ Composite

4.9.1 X-Ray Diffraction Analysis

X-ray diffraction analysis of both 20% and 40% ZrO$_2$ doped hexacelsian showed that ZrO$_2$ was retained in its tetragonal form. Hexacelsian peaks were also intact. This shows that ZrO$_2$ does not dissolve in hexacelsian and so it can be further studied for the development of composites. Fig. 4.12(a-c) shows the X-ray diffraction patterns of hexacelsian, 20% doped hexacelsian and 40% doped hexacelsian heated to 1500°C for 8 hour

4.9.2 Electron Probe Micro Analysis

Qualitative analysis showed the presence of a peak at 88.91, confirming the presence of barium, peak at 90.66 showing the presence of aluminium, peak at 77.46 showing the presence of silicon and a peak at 194.43 confirming the presence of zirconium. The result of the qualitative analysis are shown in Fig. 4.13 (a&b). Mapping was also done using EPMA to see the distribution of various elements and the micrograph used for the mapping studies are shown in Fig 4.14 (a-e). From the micrograph it appears that most of the celsian phase nucleated around ZrO$_2$ particles giving the indication of heterogeneous nucleation in these composites. However, in some places isolated nucleation sites of celsian could be seen at higher magnification (Fig. 4.14 (f)).

4.10 Stabilization of Monoclinic Celsian

4.10.1 Stabilization by TiO$_2$

Stabilization of monoclinic celsian was done by addition of TiO$_2$. Synthesis procedure was the same as that in Section 4.6 except that addition of 0.77g (5 wt% TiO$_2$) was done prior to the addition of barium acetate in the synthesis of the gel. The pellets was heated at 1500°C for 8 hours. The pellet was subjected to X-ray diffraction and SEM. X-ray diffraction analysis
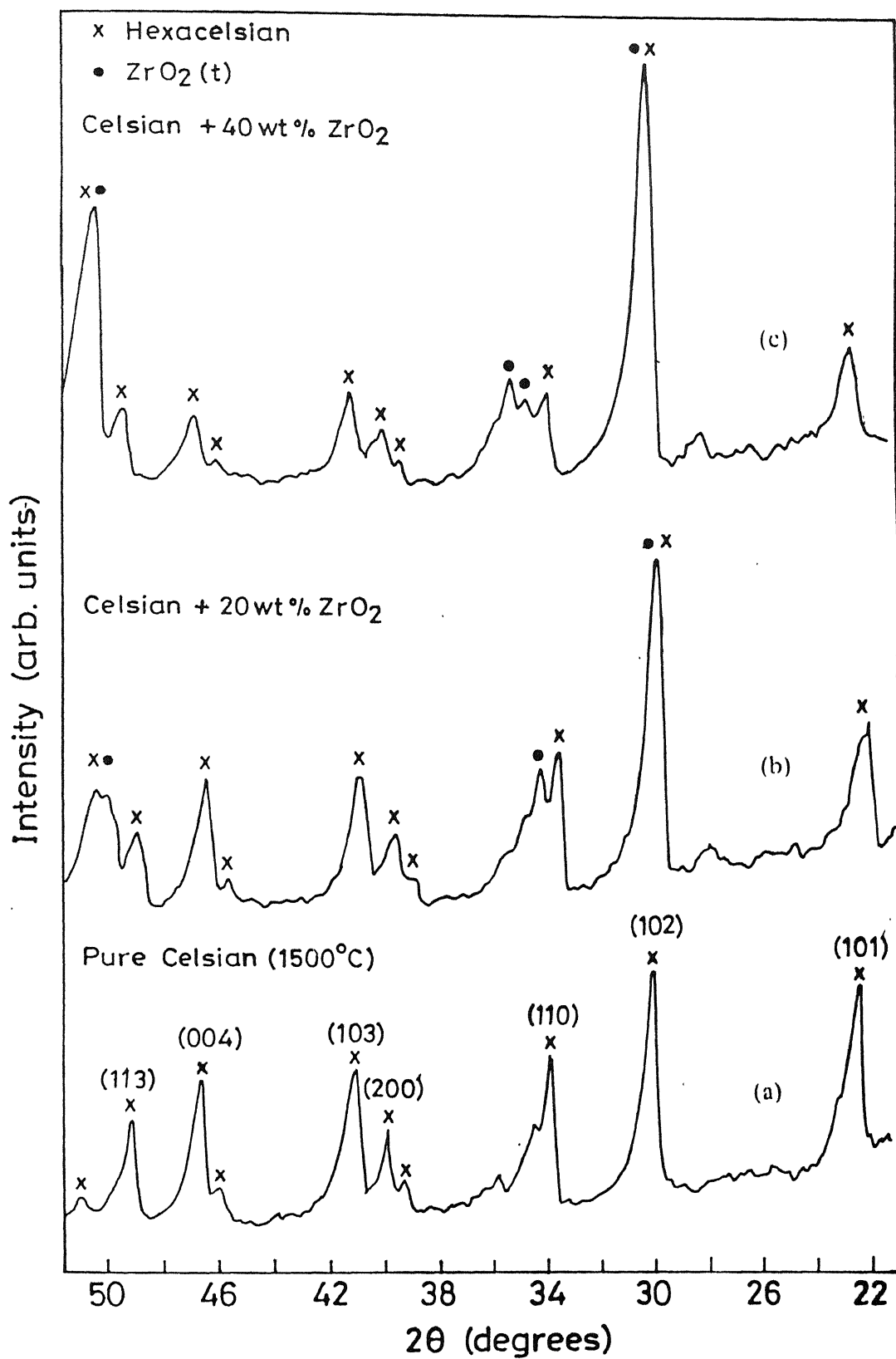
Fig 4.12: X–Ray Diffraction Patterns of (a) Hexacelsian (b) Hexacelsian + 20% ZrO_2 (c) Hexacelsian + 40% ZrO_2
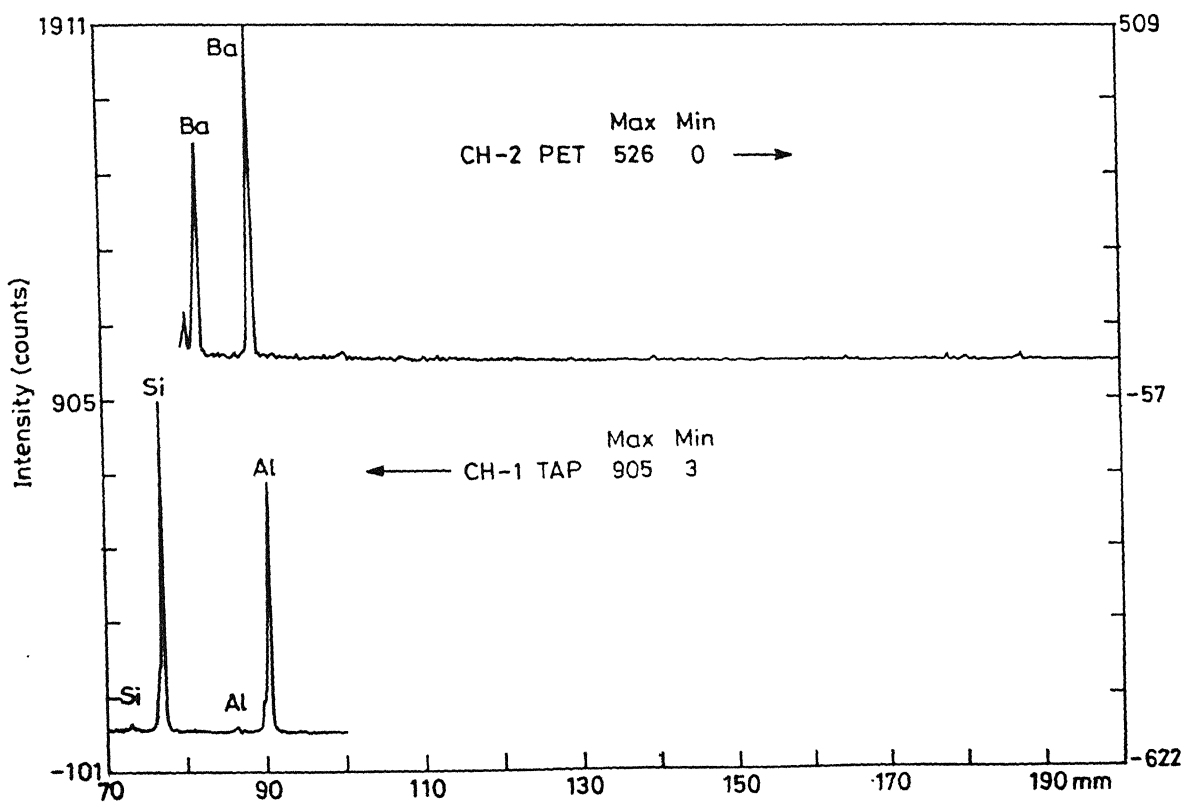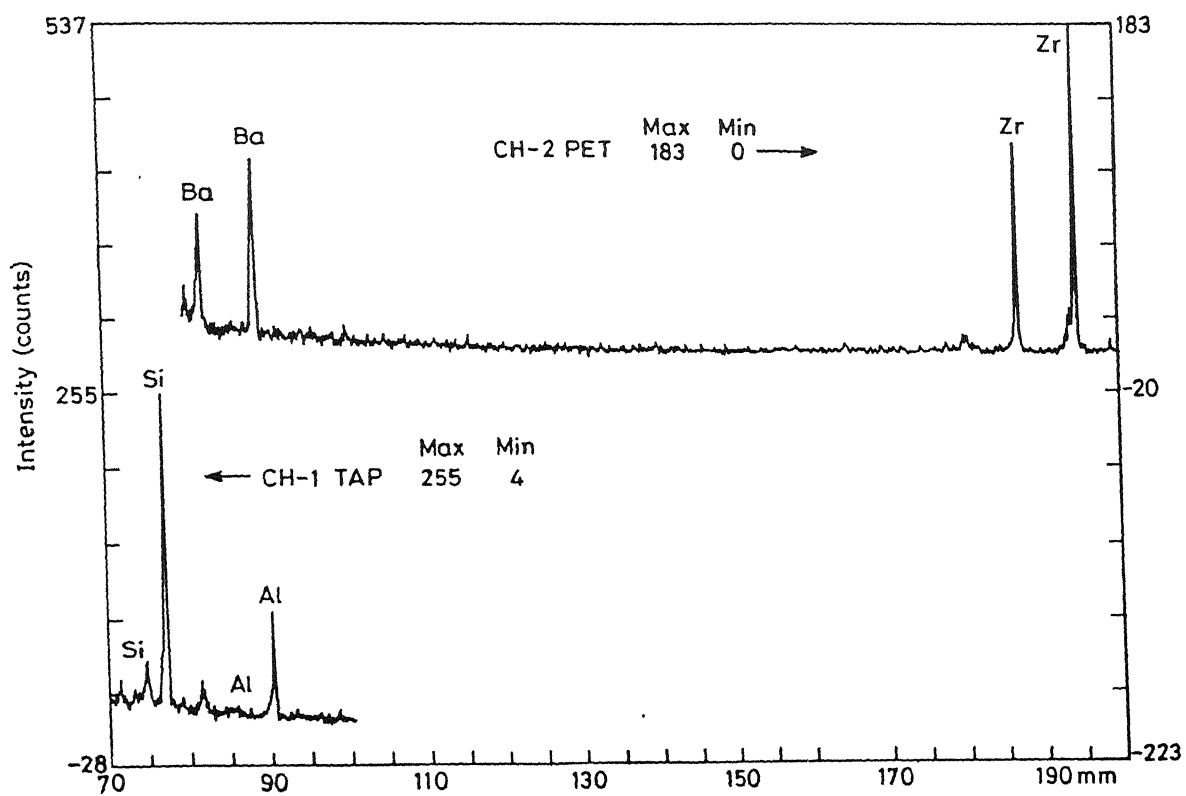
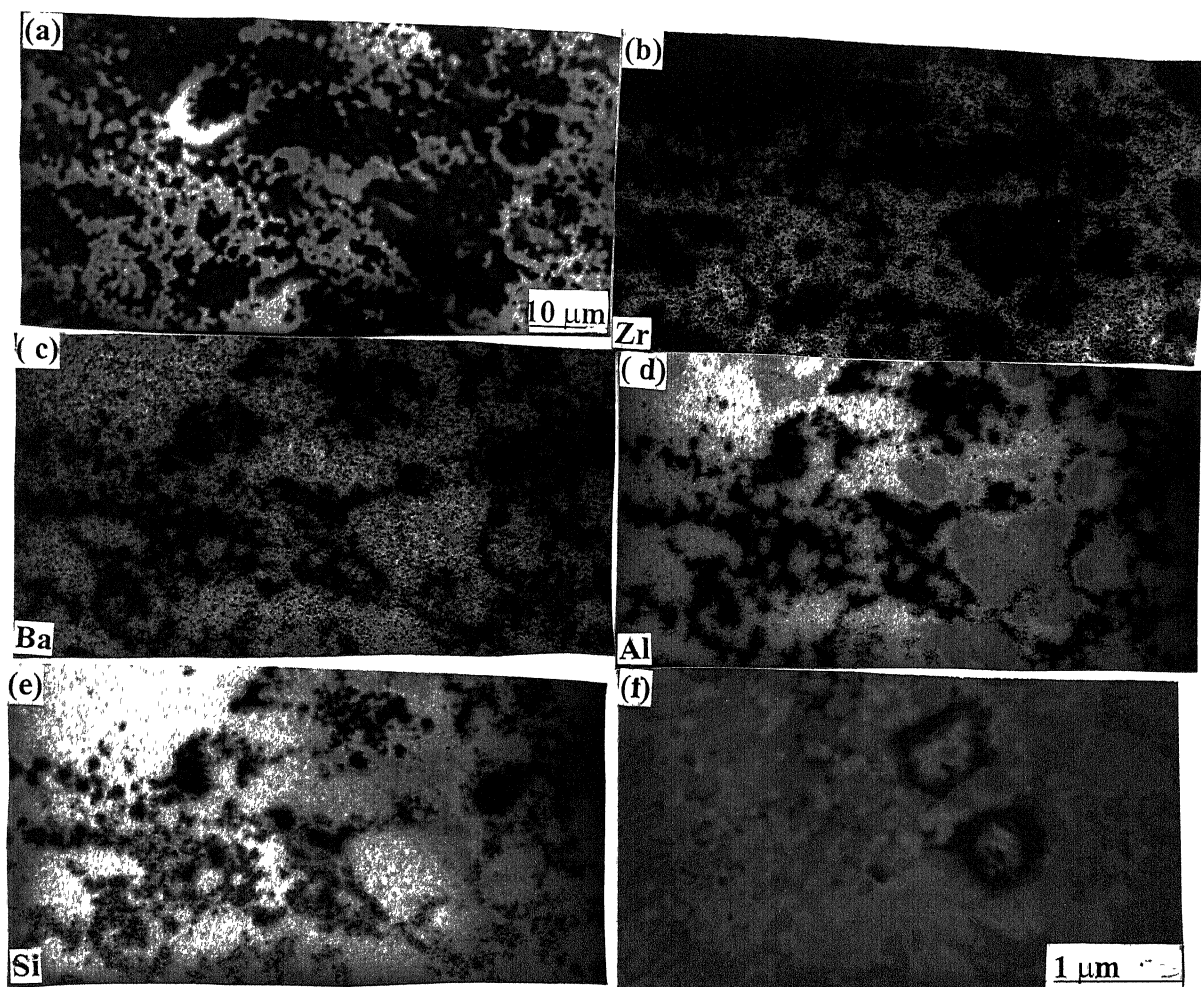Fig 4.13: EPMA Analysis Spectrum of $BaAl_2Si_2O_8 + 40\%$ ZrO_2

Fig 4.14 EPMA Analysis of Celsian-ZrO₂ Composites (a) Secondary Electron Micrograph
(b) Zr Mapping (c) Ba Mapping (d) Al Mapping (e) Si mapping (f) Celsian-ZrO₂ Composites at
a Higher Magnification indicating Heterogeneous Nucleation around ZrO₂ Particles.

showed the formation of monoclinic celsian. Fig 4.15(a) shows the X-ray diffraction pattern of monoclinic celsian formed by the addition of TiO_2. Fig 4.16 shows the formation of fine grain monoclinic celsian.

4. 10. 2 Stabilization by Li_2O

Stabilization was done by the addition of Li_2O in the form of $LiOC_3H_7$. 0.29g of $LiOC_3H_7$ (10 wt% Li_2O) was added to the gel prior to the addition of barium acetate in the synthesis as described in Section 4.6. Pellets were heated at 1300°C for 8 hours. Pellets were then subjected to X-ray diffraction and an analysis of the X-ray diffractogram showed the formation of monoclinic celsian. Fig 4.15(b) shows the X-ray diffraction pattern of monoclinic celsian obtained by using Li_2O as the chemical additive.

4. 10. 3 Stabilization by SrO_2

Stabilization was done by the addition of SrO_2 in the form of $SrCO_3$. To 1g of the synthesized gel (Section 4.6) we add 0.3g of $SrCO_3$. The powders were pelletized using a ½ inch die. This pellet was then heated at 1500°C for 8 hours and was subjected to X-ray diffraction. X-ray diffraction analysis showed the formation of monoclinic celsian. Fig 4.15(c) shows the X-ray diffraction pattern of monoclinic celsian obtained by using SrO_2 as the chemical additive.

TiO_2 is responsible for the stabilization of the monoclinic celsian because of the close structural relationship of celsian with TiO_2. The epitaxial relation between monoclinic celsian (Cn) and rutile (Ru) is $(101)_{Cn}$ // $(001)_{Ru}$, $[010]_{Cn}$ // $[110]_{Ru}$ and $[101]_{Cn}$ // $[\bar{1}01]_{Ru}$. Therefore rutile acts as the epitaxial substrat for monoclinic celsian. An additional effect is that the Ti content may also lower the viscosity of the gel matrix adjacent to the rutile seed. When the TiO_2 seeded gel was heated at 1500°C for 8 hours, monoclinic celsian could have formed directly from the epitaxial growth of amorphous matrix on the seeds[13].

The stabilization effect of Li_2O on celsian crystallization in celsian gel was attributed to a reduced viscosity (lower T_g) in the presence of Li_2O. It has been suggested that by adding Li_2O, the formation of monoclinic celsian can be achieved while preventing hexacelsian

formation, because monoclinic celsian could nucleate directly in the bulk. Addition of Li_2O to the gel promotes volume nucleation.

The stabilization of monoclinic celsian by the addition of SrO_2 is due to reaction of $SrCO_3$ with the gel forming a different phase which can act as a heterogenous centre for the crystallization of monoclinic celsian[13,14].

4.11   Grain Size determination

Grain size of monoclinic celsian stabilized by each of the chemical additive was calculated by using the formula as shown in Section 4.5. The symmetrical peak at [$\overline{2}$42] was used for the calculation of grain size. Table 4.2 shows the grain size of each of these celsians. Grain size was found to be lesser than that of hexacelsian.

Table 4.2 Grain Size of Monoclinic Celsian formed by using Various Chemical additives

Monoclinic Celsian Stabilized by	Particle Size (nm)
TiO_2	41.45
Li_2O	41.47
SrO_2	41.47

4.12   Discussion

In this study we have standardized the preparation and characterization of hexacelsian. When chemical additives like TiO_2, Li_2O and SrO_2 were added monoclinic phase crystallized. The presence of monoclinic celsian was confirmed by X-ray diffraction analysis. The main reason for the sabilization of monclinic celsian is either the close structural relationship of the additive with the celsian phase or the additive acting as a heterogeneous centre for the crystallization of monoclinic phase. ZrO_2 was added to hexacelsian to improve the toughness. When ZrO_2 was added to hexacelsian and sintered at $1500^\circ C$ for 8 hours, ZrO_2 was intact. Additionally, it was present in the tetragonal form, which was confirmed by X-ray diffraction analysis. The main aim of this part of thesis was to synthesize monoclinic celsian for developing composites with ZrO_2 and to study the mechanical properties but due to lack of time this could not be achieved.
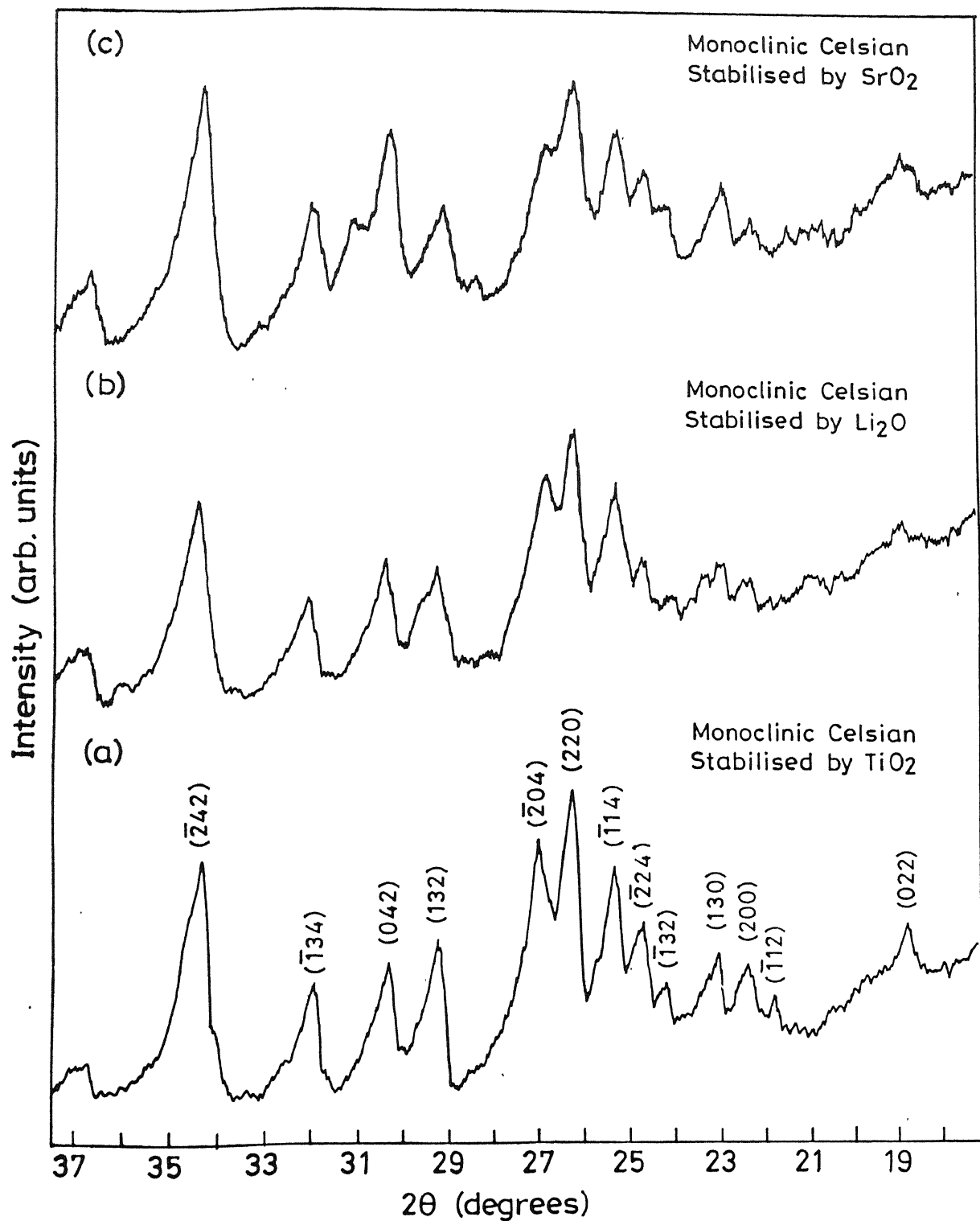
Fig 4.15: X-Ray Diffraction Pattern of Monoclinic Celsian Stabilised by (a) TiO_2 (b) Li_2O (c) SrO_2
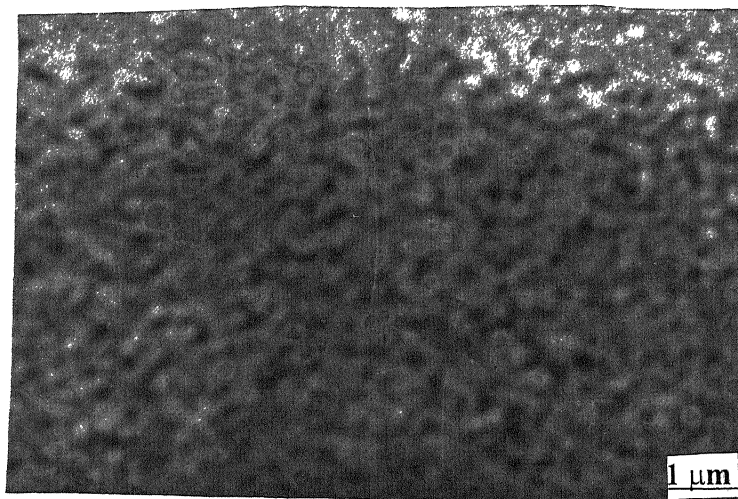
Fig 4.16: SEM Micrograph of Monoclinic Celsian Stabilized by TiO$_2$

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Chapter 5

Conclusions

1 Crosslinked polysilastyrene, crosslinked poly(tetramethyl-disilylene-co-styrene) and crosslinked polydimethylsilane were synthesized in a single step using divinylbenzene as the crosslinking agent.

2 The structure of these polymers were elucidated keeping in mind that a disilyl radical is mainly responsible for polymer propagation and also from the knowledge that silyl radicals are more reactive than styryl radicals.

3 Pyrolysis of these polymers at 1500 °C for 8 hours resulted in the formation of β-SiC. The fomation of β-SiC was confirmed by characterization techniques like X-ray diffraction, electron micro probe analysis, Raman spectroscopy and electron microscopy. From X-ray diffraction analysis, the grain size of SiC was estimated to be 8-20 nm after pyrolysis.

4 Preparation of hexacelsian by a sol-gel method was standardized. Chemical additives like TiO_2, Li_2O or SrO_2 were added during synthesis leading to the stabilization of monoclinic celsian which was confirmed by X-ray diffraction analysis. The stabilization of monoclinic celsian by these chemical additives is expected to be either due to a close structural relationship with celsian or due to the additive acting as a heterogeneous centre for the crystallization of monoclinic celsian.

5 ZrO_2 was added to hexacelsian with an intention of improving the toughness of hexacelsian. Characterization techniques like scanning electron microscopy and X-ray diffraction analysis showed that ZrO_2 did not dissolve and it was retained in the tetragonal form thus indicating that it can be effective in improving the strength of hexacelsian. Further studies are required to confirm this.

Chapter 6

Scope for Future Work

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1. Doping of SiC precursors with Zr and Ti containing additives to increase the high temperature stability of the ceramic formed.

2. Melt spinning of the polysilane precursors (crosslinked with DVB) so as to be able to generate β-SiC fibers.

3. Further studies on mechanical properties of celsian–ZrO_2 composites.

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